





# **9TH INTERNATIONAL CONFERENCE ON CHEMICAL KINETICS**

Abstract book



June 28th – July 2nd, 2015, Ghent, Belgium

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- Kevin M. Van Geem, Chair Ghent University
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- Marie-Françoise Reyniers Ghent University
- Maarten Sabbe Ghent University
- Joris Thybaut Ghent University

## Program

## Program - Sunday, June 28 & Monday, June 29

## Sunday, June 28

18.00	Registration and Welcome Reception	Lobby and Kapittel Room
Mond	ay, June 29	
07.30	Registration	Lobby
08.30	Welcome and Official Opening <b>Rik Van de Walle, Dean of the Faculty of Engineering and Architecture</b>	Main Room
08.40	Chair: William H. Green, USA Plenary Lecture 1: Quantum mechanical kinetics of gas-phase reactions (PL1) Donald Truhlar, USA	Main Room
09.40	Coffee Break	Kapittel Room

**Parallel Oral Presentations - Session 1** 

	Thermal Deomposition Main Room Chair: Kevin Van Geem, Belgium	Fundamental Kinetic Theory Room Vermeylen Chair: MF. Reyniers, Belgium	Experimental Studies Room Prior Chair: Craig Taatjes, USA
10.00	Thermal decomposition of pentadienes: The effect of resonance stabilization on the kinetics (O1) Isabelle Weber, Germany	Global uncertainty analysis for RRKM/master equation based kinetic predictions: A case study of ethanol decomposition ( <b>O7</b> ) Lili Xing, China	Experimental investigation of the oxidation of dimethyl ether in a jet-stirred reactor with PTR-TOF- MS, GC and CRDS diagnostic <b>(012)</b> <b>Michael K.M. Ward, France</b>
10.25	The effect of alcohol and carbonyl functional groups on the competition between unimolecular decomposition and isomerization in $C_1$ - $C_5$ alkoxy radicals <b>(O2)</b> <b>Enoch E. Dames, USA</b>	Spin inversion and spin selection in the reactions $Fe^+ + N_2O$ and $FeO^+ + H_2$ (O8) Jürgen Troe, Germany	A novel way to measure surface composition of solid materials by heterogeneous titration using reactive probe gases (013) Michel J. Rossi, Switzerland
10.50	Decomposition pathways of important ketohydroperoxide molecules <b>(O3)</b> Judit Zádor, USA	Rate calculation rules for automated generation of detailed kinetic models for heterocyclic compounds ( <b>O9</b> ) Fariba Seyedzadeh Khanshan, USA	Direct observation of ketohydro- peroxide formation and decomposition in photolytically initiated oxidation of <i>n</i> -butane, neopentane and diethylketone <b>(O14)</b> <b>Arkke Eskola, USA</b>
11.15	Experimental study of 3-pentanone pyrolysis and oxidation <b>(O4)</b> <b>Mohammad Aghsaee, Germany</b>	Collisional energy transfer during complex reactions in multi- component mixtures <b>(O10)</b> <b>Michael P. Burke, USA</b>	A comparative study of benzene oxidation in lean-to-rich laminar premixed flames ( <b>O15</b> ) <b>George Skevis, Greece</b>
11.40	Initial stages of the pyrolysis of polyethylene <b>(O5)</b> <b>Vadim D. Knyazev, USA</b>	Theoretical challenges in oxidation chemistry of medium-sized molecules <b>(O11)</b> <b>Ewa Papajak, USA</b>	Reaction $CH_3 + CH_3 \rightarrow C_2H_6$ studied over the 292 – 714 K temperature and 1 – 100 bar pressure ranges <b>(O16)</b> Lev N. Krasnoperov, USA
12.05	Stochastic kinetic modelling of the of polyethylene pyrolysis <b>(O6)</b> <b>Francisco Lemos, Portugal</b>		High-temperature autoignition study of furan and tetrahydro- furan ( <b>O17</b> ) <b>Ben Akih-Kumgeh, USA</b>

12.30 Lunch Break

**Kapittel Room** 

Chair: Craig Taatjes, USA
 14.00 Plenary Lecture 2: Interesting kinetics at low, medium and high temperatures (PL2)
 Paul Seakin, UK

Main Room

## Program - Monday, June 29

Parallel Oral Presentations - Session 2

	Renewable Fuel Chemistry Main Room Chair: C. F. Goldsmith, USA	Catalysis Modeling Room Vermeylen Chair: Guy Marin, Belgium	Ab Initio Modeling Room Prior Chair: Judit Zádor, USA
15.00	Influence of oxygenation in cyclic hydrocarbons on chain- termination reactions from $R + O_2$ : Tetrahydropyran and cyclohexane <b>(O18)</b> <b>Brandon Rotavera, USA</b>	Surface reaction kinetics of steam- and $CO_2$ -reforming as well as oxidation of methane over Ni, Rh, Pt-based catalysts ( <b>O24</b> ) <b>Olaf Deutschmann, Germany</b>	Combustion chemistry via meta- dynamics: Benzyl decomposition revisited (O29) Daniela Polino, Switzerland
15.25	A low pressure flame study of 2-butyltetrahydrofuran ( <b>O19</b> ) Alena Sudholt, Germany	CO <sub>2</sub> methanation: Catalyst synthesis and kinetics <b>(O25)</b> Franz Koschany, Germany	A theoretical and experimental investigation of the reaction of O( <sup>3</sup> P) with propene and propyne <b>(O30)</b> <b>Carlo Cavallotti, Italy</b>
15.50	The multichannel reaction of O( <sup>3</sup> P) with cyclopentene <b>(O20)</b> John D. Savee, USA	The critical role of water in cata- lytic CO oxidation over Au/TiO <sub>2</sub> catalysts ( <b>O26</b> ) Lars Grabow, USA	Theoretical analysis of the effect of C=C double bond on the fate of alkenylperoxy radicals <b>(031)</b> <b>Xiaoqing You, China</b>
16.15	Computational study of the cyclopentyl + $O_2$ and methyl- cyclopentyl + $O_2$ reactions ( <b>O21</b> ) <b>Mariam El Rachidi, Saudi</b> <b>Arabia</b>	Pt clusters in LTA zeolite for hydrogen combustion in hydrocarbon rich conditions ( <b>O27</b> ) <b>Yu-Ling Shan, China</b>	A systematic study of radical addition reactions to substituted benzenes and the reverse beta- scission reactions (O32) Hans-Heinrich Carstensen, Belgium
16.40	A high temperature experimental and theoretical kinetic study for the reaction of tetrahydrofuran with hydroxyl radicals (O22) Binod Raj Giri, Saudi Arabia	Assessment of catalytic performance for oxidative coupling of methane via comprehensive microkinetic modelling <b>(O28)</b> Joris Thybaut, Belgium	<i>Ab initio</i> quantum chemical reaction kinetics: Recent applications in combustion chemistry <b>(033)</b> <b>Ghanshyam L. Vaghjiani, USA</b>
17.05	Development of an optimized ethanol combustion mechanism (O23) Carsten Olm, Hungary		Rate constants from elementary reactions may fail for combustion kinetic studies (O34) João Brandão, Portugal

17.30 Poster Session 1 (even poster numbers): Belgian beer night and snacks

Kapittel Room

## Program - Tuesday, June 30

08.30	Welcome and Poster Prize	Main Room
08.40	Chair: Marie-Françoise Reyniers, Belgium Plenary Lecture 3: Electrostatic catalysis of non-redox reactions (PL3) Michelle Coote, Australia	Main Room
09.40	Coffee Break	Kapittel Room

## Parallel Oral Presentations - Session 3

	First Principles Modeling Main Room Chair: Carlo Cavallotti, Italy	Process Catalysis Room Vermeylen Chair: O. Deutschmann, Germany	Atmospheric & Aerosol Chemistry Room Prior Chair: Dagmar D'hooge, Belgium
10.00	Reactions of NH <sub>2</sub> with formal-dehyde, hydrogen peroxide and hydrazine: A challenge to theory <b>(O35)</b> <b>Paul Marshall, USA</b>	Experimental design in non linear case applied to hydrocracking model: How many points do we need and which ones? <b>(O41)</b> <b>Benoit Celse, France</b>	On the reaction of RO <sub>2</sub> radicals with OH radicals <b>(047)</b> <b>Christa Fittschen, France</b>
10.25	Direct dissociation of excited radicals is important in combustion modeling <b>(O36)</b> <b>Claude Franklin Goldsmith, USA</b>	Reactor optimization for maximized propene yields in olefins cracking on ZSM-5 using single-event methodology <b>(O42)</b> <b>Tassilo von Aretin, Germany</b>	Thermochemical closure of uptake and evaporation kinetics of $H_2O$ , $HNO_3$ and HCl on atmospheric ices in the range 170 to 210 K <b>(O48)</b> <b>Michel J. Rossi, Switzerland</b>
10.50	Chain branching in cyclo- pentadienone oxidation and thermochemistry for the alcohols, hydroperoxides, vinylic, alkoxy and alkylperoxy radicals ( <b>O37</b> ) Joseph W. Bozzelli, USA	Composition and formation kinetics of green oil in selective acetylene hydrogenation over a commercial Pd-Ag/Al <sub>2</sub> O <sub>3</sub> catalyst <b>(O43)</b> <b>Jian Zhang, China</b>	Direct kinetic measurements of the reactions of the simplest Criegee Intermediate CH <sub>2</sub> OO with alkenes and carbonyl compounds <b>(O49)</b> <b>Rehab M.I. Elsamra, USA &amp;</b> <b>Egypt</b>
11.15	Unraveling the competing pathways in the reaction of hydroxyl with 2-butene <b>(O38)</b> Leonid Sheps, USA	Modeling the removal of sulfur, aromatics and heavier fraction of scrap tire pyrolysis oil (STPO) <b>(O44)</b> Idoia Hita, Spain	Yields of nitric acid and peroxynitrous acid products in the HO <sub>2</sub> + NO reaction detected by Cavity Ringdown Spectroscopy <b>(O50)</b> <b>Mitchio Okumura, USA</b>
11.40	Computational kinetic study on ROO to QOOH reactions in 2-MTHF oxidation <b>(O39)</b> <b>Prajakta R. Parab, Germany</b>	Liquid kinetic study of the catalytic cracking of waste motor oil for obtaining diesel like fuels in a batch process <b>(O45)</b> <b>Diana Vargas, Ecuador</b>	A kinetic study of the CH <sub>2</sub> OO Criegee Intermediate uni- molecular reaction and bimolecular reactions with CH <sub>2</sub> OO, SO <sub>2</sub> and halogenated carboxylic acids using Cavity Ringdown Spectroscopy <b>(O51)</b> <b>Rabi Chhantyal-Pun, UK</b>
12.05	Kinetic isotope effect of $C_2H_6$ + OH and $C_2D_6$ + OH: Experimental and theoretical study <b>(O40)</b> <b>Binod Raj Giri, Saudi Arabia</b>	Bifurcational parametric simplification in chemical kinetics <b>(046)</b> Gregory Yablonsky, USA	Reaction kinetics of homogeneous transformations of guaiacol in urban wet aerosol particles <b>(O52)</b> Ana Kroflič, Slovenia
12.30			Kinetic studies of the atmospherically implicated halogen oxide radical and peroxy radical cross-reactions (053) Michael K. M. Ward, France

#### 12.30 Lunch

#### **Kapittel Room**

Chair: Guy Marin, BelgiumMain Room14.00Plenary Lecture 4: Descriptors of reactivity and selectivity in chemical reactions catalyzed by solids (PL4)Enrique Iglesia, USA

## Program - Tuesday, June 30

**Parallel Oral Presentations - Session 4** 

	Catalysis Kinetics Main Room Chair: Joris Thybaut, Belgium	Combustion & Oxidation Models Room Vermeylen Chair: Michael Harper, USA	Molecular Growth Modeling Room Prior Chair: HH. Carstensen, Belgium
15.00	Revisiting the kinetics of selective hydrogenation of phenylacetylene over an egg-shell catalyst <b>(054)</b> <b>Zhiming Zhou, China</b>	Kinetic study of the pyrolysis and oxi- dation of unsaturated alcohols <b>(O59)</b> <b>Ruben De Bruycker, Belgium</b>	Kinetic modeling of carbon black formation <b>(O65)</b> <b>Simple Kumar, India</b>
15.25	Experiments and modeling of after- treatment options for alternative fuel based engines <b>(O55)</b> <b>Snigdha sree Ramireddy, India</b>	Reaction of CH <sub>3</sub> radicals with HO <sub>2</sub> (O60) Chao Yan, USA	Kinetics of naphthalene formation via HACA pathways <b>(O66)</b> <b>Stephen J. Klippenstein, USA</b>
15.50	Kinetics of catalytic carbon gasification: Kinetic linearity, 'carbonworms', 'casa' front <b>(O56)</b> Luis Sousa Lobo, Portugal	Development of a joint hydrogen and syngas combustion mechanism based on an optimization approach ( <b>061</b> ) <b>Carsten Olm, Hungary</b>	Experimental kinetic study of several reactions critical to PAH formation: Vinyl + 1,3-butadiene, vinyl + acetylene and phenyl + acetylene ( <b>O67</b> ) <b>Zachary J. Buras, USA</b>
16.15	How to apply the method of moments for polymerization reactions to the Fischer Tropsch Synthesis (FTS) <b>(057)</b> Luis A. Lozano Guerra, Belgium	Energy diagrams of OOQOOH and detailed chemical kinetics modeling on the low-temperature oxidation of diethyether <b>(O62)</b> <b>Yasuyuki Sakai, Japan</b>	A new pathway to form naphthalene from the addition of fulvenallenyl and propargyl radicals: A quantum chemistry/ master equation study <b>(O68)</b> <b>Edward Ross, Australia</b>
16.40	Kinetic investigation of the anaerobic bio-digestion process of organic wastes from the agribusiness (O58) Daniela Almeida Streitwieser, Ecuador	Detailed chemical kinetic modeling study of isobutene oxidation: Ignition delay time <b>(O63)</b> <b>Chong-Wen Zhou, Ireland</b>	The strength of model-based design for nitroxide mediated polymerization <b>(O69)</b> <b>Dagmar D'hooge, Belgium</b>
17.05		High temperature kinetic mechanism development of 2-phenyl ethanol combustion from ignition delay time measurements in a shock tube (O64) Vijai Shankar Bhavani Shankar, Saudi Arabia	Determining rubber composition of waste tires using devolatilization kinetics (070) Bart Danon, South Africa

17.30 Poster Session 2 (uneven poster numbers): Belgian beer night and snacks

Kapittel Room

## Program - Wednesday, July 1

08.30	Welcome and Poster Prize	Main Room
08.40	Chair: Kevin Van Geem, Belgium Keynote Lecture 1: Recent advances (and continuing challenges) in combustion chemistry (KL1) William H. Green, USA	Main Room

09.20 Coffee Break

**Kapittel Room** 

#### **Parallel Oral Presentations - Session 5**

	Automated Mechanism Generation Main Room Chair: William H. Green, USA	Solution & Liquid Phase Kinetics Room Vermeylen Chair: Michel J. Rossi, Switzerland
09.50	Automatic kinetic calculations for reaction mechanism generation (071) Pierre L. Bhoorasingh, USA	Mechanism of the oxidation of 1-(ferrocenyl)– ethanone/ethanol by dicyanobis(phenanthroline) iron(III) (077) Rozina Khattak, Pakistan
10.15	3D automatic kinetic model generation <b>(072)</b> Ruben Van de Vijver, Belgium	Quenching processes under restricted geometry conditions: A quantitative treatment ( <b>078)</b> <b>Manuel López-López, Spain</b>
10.40	Improving kinetic models for alcohol combustion: An iso-butanol case study <b>(073)</b> Samah Y. Mohamed, Saudi Arabia	Peculiarities of the reactions between early lanthanide(III) ions and an anionic porhyrin <b>(O79)</b> Zsolt Valicsek, Hungary
11.05	AramcoMech: A hierarchal chemical kinetic model for hydrocarbon fuels <b>(074)</b> Mani Sarathy, Saudi Arabia	Oxidation of pyruvic acid and lactic acid by OH radicals in aqueous solution <b>(080)</b> Thomas Schaefer, Germany
11.30	Characterizing Ignition behavior through morphing to generic curves <b>(075)</b> Edward S. Blurock, Sweden	Tropospheric aqueous-phase oxidation of isoprene degradation products <b>(O81)</b> <b>Tobias Otto, Germany</b>
11.55	Reaction pathway analysis of ReaxFF MD simulations with VARxMD <b>(076)</b> Xiaoxia Li, China	Recent advances in studying the mechanism of phospha-Michael addition of tertiary phosphines to electron-deficient alkenes <b>(O82)</b> <b>Alexey V. Salin, Russia</b>

Chair: William H. Green, USA

Main Room

12.20 Keynote Lecture 2: CloudFlame and PrIMe: Accelerating combustion research in the cloud (KL2)
 Mani Sarathy, Saudi Arabia

13.00 Lunch

Kapittel Room

14.00 Departure to Bruges

22.00 Departure in Bruges

## **Program - Thursday, July 2**

08.30 Welcome and Introduction of MaCKiE

 Chair: Ingmar Nopens, Belgium
 Main Room

 08.40
 Plenary Lecture 5: On the detailed modelling of high temperature nanoparticles synthesis (PL5)

 Markus Kraft, UK

09.40 Coffee Break

#### Kapittel Room

**Main Room** 

#### **Parallel Oral Presentations - Session 6**

	CFD with Detailed Kinetics Main Room Chair: Rodney Fox, USA	Catalysis Meets Mathematics Room Vermeylen Chair: Xing-Gui Zhou, China	Mathematics for chemical kinetics Room Blanquaert Chair: Denis Constales, Belgium
10.00	CFD simulations of iso-octane ignition in rapid compression machines using detailed chemistry (O83) Nicolas Bourgeois, Belgium	Mathematics of mixed gases adsorbed in a zeolite ( <b>O90</b> ) <b>Dezheng Wang, China</b>	A heterogeneous multi-scale dynamic model for simulation of catalytic reforming reactors <b>(O97)</b> <b>Grigorios Pantoleontos, Greece</b>
10.25	Improving laboratory reactors: Computational fluid dynamics and detailed chemical kinetics ( <b>084</b> ) <b>Pieter A. Reyniers, Belgium</b>	New active sites or old surface species? A methodology to understand the kinetics behind dynamic behavior of gas-solid catalytic reactions using feed switching experiments <b>(O91)</b> <b>Sam Wilkinson, UK</b>	Efficient method for the calculation of rate coefficients of elementary reactions in the gas phase ( <b>O98</b> ) Andrey Koksharov, Germany
10.50	An approach to develop a kinetic model from a stirred tank reactor accounting for the role of hydrodynamics: (+)-Nootkatone bioconversion <b>(085)</b> <b>Carlos Castillo-Araiza, Mexico</b>	Steady-state and transient kinetic studies on the palladium catalyzed acetoxylation of toluene <b>(O92)</b> Sven Reining, Germany	New observation of water gas shift equilibrium in flames <b>(O99)</b> <b>Gregory Yablonsky, USA</b>
11.15	Detailed microkinetics and the mathematics of diffusion and shape selective catalysis <b>(086)</b> <b>Dezheng Wang, China</b>	Microkinetic modeling of steady state isotopic transient kinetic analysis data for fischer-tropsch synthesis <b>(093)</b> Jonas Van Belleghem, Belgium	On reactive settling of activated sludge <b>(0100)</b> Raimund Bürger, Chile
11.40	CFD-based design of 3D pyrolysis reactors (087) David J. Van Cauwenberge, Belgium	Study of gas-liquid photocatalytic kinetics via a compact photomicroreactor assembly <b>(O94)</b> Yuanhai Su, The Netherlands	Probing pore blocking effects on multiphase reactions at the particle level using a discrete model (O101) Guanghua Ye, China
12.05	Numerical simulations of steam cracking test furnace using detailed combustion mechanism for CO and NOx emission <b>(O88)</b> <b>Yu Zhang, Belgium</b>	Variable activation energies during heterogeneous catalysis ( <b>O95</b> ) <b>Trevor C. Brown, Australia</b>	Parameter fitting: Which algorithm to choose? <b>(O102)</b> Benoît Celse, France
12.30	Non-linear regression of the thermochemical state-space onto a reduced number of principal components <b>(089)</b> Alessandro Parente, Belgium	Rate-Reactivity Model (RRM): A new basis for non-steady- state kinetic characterization of heterogeneous catalysts <b>(096)</b> <b>Gregory Yablonsky, USA</b>	A comparative study of optimization algorithms for a cellular automata model <b>(O103)</b> Saurajyoti Kar, India

12.55 Closure of ICCK'15 Kevin Van Geem, Chair of the Local Organizing Committee Main Room

13.00 Lunch for MaCKiE participants

14.00 Start of MaCKiE

Kapittel Room

## Poster List

## **Aerosol/ Heterogeneous Kinetics**

P1 Kinetics of O3 uptake onto indoor surfaces and secondary VOC emissions in a classroom Michael K. M. Ward, M. Mendez, S. Gosselin, N. Visez, C. Schoemaecker (France)
P2 Stability of iprodione in AOT-based reverse micelles under alkaline conditions
J. Morales, A Cid, O. Moldes, Juan C. Mejuto (Spain & Portugal)

## Astrochemistry

## P3 Reaction of OH radicals with small oxygenates in the gas phase: Kinetic study at ultralow temperatures

Maria Antiñolo, E. Jiménez, B. Ballesteros, A. Canosa, J. Albaladejo (Spain & France)

## **Biocatalysis / Enzyme Kinetics**

## P4 Mechanistic role of the second and third coordination sphere of cysteine dioxygenase

Casey G. Davies, E. P. Tchesnokov, M. Fellner, S. M. Wilbanks, G. N. L. Jameson (New Zealand)

## Catalysis

# P5 Green chemistry in oxidation: Catalytic activation of hydrogen peroxide by transition on metals for oxidation reactions

Ahmad M. Al-Ajlouni, R. Marji (Saudi Arabia & Jordan)

P6 The kinetics and mechanism of the oxidation of brilliant green by carbonate ion in the presence of some cationic surfactants

Oladega O. Soriyan, G. O. Ogunlusi, O. Owoyomi, A. Adegoke (Nigeria)

## P7 A DFT study of adsorption of ethane on oxygen-covered platinum clusters

Peter Kraus, P. Lindstedt (UK)

# P8 The art of developing a kinetic model during the design of an industrial packed bed reactor: Oxidative dehydrogenation of ethane to ethylene on MoVTeNbO/TiO2 catalyst

G. Che-Galicia, R.S. Ruiz-Martínez, F. López-Isunza, Carlos O. Castillo-Araiza (Mexico)

### P9 Co-processing of waste plastic and hydrocarbons over HZSM-5

N. Carmo, D. Afonso, E. Santos, I. Fonseca, F. Lemos, Maria Amalia Lemos (Portugal)

### P10 Stability of humate aggregates in presence of pesticides

J. Morales, A Cid, O. Moldes, Juan.C. Mejuto (Spain & Portugal)

## P11 Kinetics of phenol hydrodeoxygenation over a NiMo/γ-Al2O3 catalyst

A. Papastylianou, Ch. Templis, Nikos Papayannakos (Greece)

## P12 Experimental study of catalytic coating for reduced coke formation

Stamatis A. Sarris, C. M. Schietekat, L. B. Kool, W. Peng, P. Lucas, K. M. Van Geem, G. B. Marin (Belgium & China)

## P13 Application of montmorillonite-Cu(II)ethylenediamine catalyst for the decolorization of Chromotrope 2R with H2O2 in aqueous solution

Ibrahim A. Salem, H. A. El-Ghamry, M. A. El-Ghobashy (Egypt)

### P14 Static and dynamic study of alkene cracking intermediates in H-ZSM-5

<u>Pieter Cnudde</u>, J. Van der Mynsbrugge, K. De Wispelaere, K. Hemelsoet, M. Waroquier, V. Van Speybroeck (Belgium)

### **Combustion Kinetics**

P15 The decomposition of hydroxyamyl and pentyloxy radicals of 2-Methyl-1-butanol: A theoretical study

X. Zhou, X. Zhang, Lidong Zhang (China)

### P16 Modelling approaches for the combustion of coke deposited on cracking catalysts

A. Ochoa, Idoia Hita, Á. Ibarra, M. Artetxe, J. M. Arandes, P. Castaño (Spain)

P17 From rich to lean conditions, dimethoxymethane oxidation modeling at high pressures

Lorena Marrodán, Á. Millera, R. Bilbao, M.U. Alzueta (Spain)

P18 Investigations on the catalytic effects of potassium and silicon in the thermo-chemical gasification of agricultural residues

Angela Hofmann, M. Huemer, D. Bozic, M.B. Huber (Austria)

P19 A single-pulse shock tube coupled with high-repetition-rate time-of-flight mass spectrometry and gas chromatography for high-temperature kinetics studies

Paul Sela, M. Aghsaee, J. Birkmann, B. Shu, J. Herzler, M. Fikri, C. Schulz, O. Welz (Germany)

P20 First-principles based group additivity values for thermochemical properties of substituted aromatic compounds

Alper Ince, H.-H. Carstensen, M.-F. Reyniers, G.B. Marin (Belgium)

P21 Photodissociation of methanol at 193.3 nm  $\underline{C}$ 

hao Yan, L. N. Krasnoperov (USA)

P22 Study of OH radical kinetics relevant for dimethylether combustion using the FAGE technique

Lavinia Onel, M. Blitz, D. Potter, P. Seakins (UK)

P23 Thermal decomposition of graphene oxyradicals under the influence of an embedded five-membered ring

H. Wang, H.-B. Zhang, M. J. Pilling, Xiaoqing You (UK)

P24 The very open data project: Characterizing combustion kinetic data with ontologies and meta-data

Edward S. Blurock (Sweden)

P25 A detailed cyclic ether oxidation mechanism for oxiranyl and 2-oxetanyl radicals: A theoretical study

H. Wang, Joseph W. Bozzelli (USA)

P26 On the reaction of isoprene hydroxyl-peroxy radicals with HO2 radicals

Emmanuel Assaf, C. Schoemaecker, C. Fittschen (France)

P27 Quantum chemical and kinetic study of the oxidation mechanisms of naphthalene initiated by hydroxyl radicals. I. The H abstraction pathway

Abolfazl Shiroudi, M. S. Deleuze (Belgium)

P28 Quantum chemical and kinetic study of the oxidation mechanisms of naphthalene initiated by hydroxyl radicals. II. The OH addition pathway

Abolfazl Shiroudi, M. S. Deleuze, S. Canneaux (Belgium & France)

## **Coupling CFD with Kinetics**

P29 Adaptive on-the-fly regression tabulation: Beyond ISAT

Edward S. Blurock (Sweden)

**Experimental Methods** 

P30 Fast pyrolysis of lignocellulosic biomass: Design and construction of a micro-pyrolysis setup for intrinsic kinetic measurements

Hilal Ezgi Toraman, H.-H. Carstensen, K. M. Van Geem, G. B. Marin (Belgium)

P31 Kinetic and thermodynamic studies of cadmium removal by adsorption on natural brown clay

Latifa Bentchikou, A. Mellah (Algeria)

P32 An experimental and theoretical study of cyclopentadiene-ethene co-pyrolysis: Growth of polycyclic aromatic hydrocarbons

Marko R. Djokic, A. G. Vandeputte, S. S. Merchant, W. H. Green, K. M. Van Geem, G. B. Marin (Belgium & USA)

P33 Understanding the decomposition of sulfur compounds during steam cracking and their influence on coke formation and product distribution

<u>Natalia Olahova</u>, M. R. Djokic, S. A. Sarris, R. Van de Vijver, M.-F. Reyniers, K. M. Van Geem, G. B. Marin (Belgium)

P34 Reactions of the simplest Criegee intermediate studied directly using a novel multipass, broadband time-resolved absorption spectrometer

Thomas R. Lewis, M. A. Blitz, D. E. Heard (UK)

### **Fundamental Kinetic Theory**

## P35 A new group additive kinetic model for pyrolysis of C2-C4 hydrocarbons

M. Khandavilli, Kevin M. Van Geem, R. Van de Vijver, G. B. Marin (Belgium)

### P36 The spin-forbidden reaction of atomic sulfur with ethylene

K. M. Thompson, Y. Gao, Paul Marshall (USA)

### **Homogenous Atmosphere Chemistry**

### P37 Gas-phase reactivity study of C3F7CH=CH2 with oh radicals, Cl atoms and ozone

Amparo Soto, B. Ballesteros, E. Jiménez, A. Moreno, S. González, J. Albaladejo (Spain)

P38 Kinetic study of the Cl and NO3-initiated photo-oxidation of unsaturated (allyl and vinyl) ethers under simulated atmospheric conditions

J. P. Aranguren Abrate, I. Colmenar, <u>Sagrario Salgado</u>, E. Martínez, B. Cabañas, P. Martín (Argentina & Spain)

## P39 Peroxy radical isomerisation and hydroxyl radical recycling in isoprene oxidation: Upgraded mechanism LIM1

J. Peeters, S. Vinh Nguyen, Jean-François Muller, T. Stravrakou (Belgium)

## P40 A computational study of the thermochemistry of N2O5 and the kinetics of the reaction N2O5 + H2O $\rightarrow$ 2 HNO3

Paul Marshall, I. M. Alecu (USA)

## P41 Tropospheric degradation of E,E-2,4-hexadienal during the day

I. Colmenar, S. Salgado, E. Martínez, B. Cabañas, Pilar Martín (Spain)

## P42 OH reactivity studies of VOC oxidation in the HIRAC chamber

Charlotte A. Brumby, D. R. Cryer, L. K. Whalley, D. E. Heard, P. W. Seakins (UK)

## P43 Kinetics of the unimolecular reaction of CH2OO and its reaction with the water monomer, acetaldehyde and acetone at atmospheric conditions

<u>Torsten Berndt</u>, R. Kaethner, J. Voigtländer, F. Stratmann, P. Reichle, M. Pfeifle, M. Olzmann, M. Sipilä, M. Kulmala, H. Herrmann (Germany & Finland)

## P44 Autoxidation of cyclohexenes in the gas-phase

Matti P. Rissanen, T. Kurtén, R. L. Mauldin III, O. Garmash, N. Hyttinen, H. G. Kjaergaard, M. Ehn (Finland, USA & Denmark)

### **Ion Kinetics**

## P45 Reduction mechanism of tellurium species from copper electro winning solutions

Mohammad Mokmeli, D. B. Dreisinger, B. Wassink (Canada)

### P46 Enthalpy values for bromine ions' hydration in aqueous solutions

G. V. Karpov, Igor I. Morozov, E. S. Vasiliev, S.V. Savilov, V.V. Lunin (Russia)

### **Solution/Liquid Kinetics**

# P47 Thermodynamic aspect: Kinetics of the reduction of dicyanobis(phen)iron(III) by acetylferrocene and methylferrocenemethanol

Rozina Khattak, I. I. Naqvi (Pakistan)

### P48 Kinetic studies in micellar systems undergoing morphological transitions

Pilar López-Cornejo, M. López-López, B. Sarrión, F. J. Ostos, M. L. Moyá (Spain)

# P49 Effects of axial ligands on the formation kinetics of water-soluble samarium(III) porphyrins

Melitta Patrícia Kiss, Z. Valicsek, O. Horváth (Hungary)

# P50 The role of water and the ligand's charge in the formation kinetics of bismuth(III) porphyrins

Zsolt Valicsek, K. Patonay, O. Horváth (Hungary)

Lecture abstracts

Plenary lectures

## Quantum mechanical kinetics of gas-phase reactions

Donald Truhlar Professor of Theoretical and Computational Chemistry, University of Minnesota Minneapolis, USA

This talk will present Multi-Path Variational Transition State Theory (MP-VTST): its background, its components, and its applications. The components include electronic structure calculations, variational optimization of multi-faceted transition states, multistructural torsional anharmonicity, anharmonicity of high-frequency modes, and multidimensional tunneling. The talk will also address the issue of fitting rate constants to a functional form as a function of temperature. Applications will be presented from the fields of biofuel combustion and plasma chemistry.

This work was supported in part by the U.S. Department of Energy.

## **Interesting Kinetics at Low, Medium and High Temperatures**

Paul Seakins Professor of Reaction Kinetics, School of Chemistry, University of Leeds, Leeds, UK

There is sometimes a perception that there is little new to discover in the field of gas phase kinetics; the interesting experiments have been done and what is left can be done more cheaply and with comparable accuracy by ab initio calculations! In this talk I want to give a much more positive view and will give some examples showing that there are still many issues to unravel and that experimental kinetics, supported by theory and calculations, has an integral role to play in solving problems with a variety of applications. The first example concerns low temperature energy transfer parameters showing how measurements at room temperature can provide elegant proof of the 'gateway mechanism' for electronic relaxation of singlet methylene, but at low temperatures, relevant for planetary atmospheres the mechanism of relaxation changes and rates increase with implications for modelling of planetary atmospheres. The second example will present recent results on OH recycling and how this can contribute to our knowledge and understanding of field observations of OH radicals in biogenic environments. Understanding OH levels in tropical regions is vital for predicting future methane levels and hence climate change. Finally we conclude with some recent work on dimethylether combustion probing the role of chemical activation and surface chemistry.

## **ELECTROSTATIC CATALYSIS OF NON-REDOX REACTIONS**

<u>Michelle L. Coote</u>,<sup>1,2\*</sup> Naomi L. Haworth,<sup>1,2</sup> Nathaniel Bloomfield,<sup>2</sup> Ganna Gryn'ova,<sup>2</sup> Marta Klinska,<sup>2</sup> Leesa M. Smith,<sup>2</sup> Martin G. Banwell,<sup>2</sup> Simone Ciampi,<sup>1,3</sup> Nadim Darwish,<sup>4</sup> and Ismael Diez-Perez<sup>4</sup> <sup>1</sup>ARC Centre of Excellence for Electromaterials Science <sup>2</sup>Research School of Chemistry, Australian National University

<sup>3</sup>Intelligent Polymer Research Institute, University of Wollongong <sup>4</sup>Departament de Química Física, Universitat de Barcelona

Keywords

catalysis, polar effects, electrostatic effects, quantum chemistry, Diels-Alder reactions, nitroxides.

It is well known that the rate of redox reactions can be manipulated by means of an electrical potential gradient. However, in this talk we will show that electrostatic catalysis is also a practical possibility for manipulating non-redox processes. As elegantly demonstrated by Shaik and co-workers, many formally covalent species can be stabilized by resonance between their covalent and one or more charge-separated mesomeric forms.<sup>1</sup> In principle, if an electric field is oriented in such a way as to electrostatically stabilize one of these minor contributors, the amount of resonance will increase and the species will be stabilized accordingly. As an example, Shaik and co-workers showed via quantum-chemical modelling that an oriented electric field (OEF) could be used to promote selectivity between the exo and endo products of a simple Diels-Alder reaction, and also lower the activation barriers.<sup>1</sup> However, for electrostatic catalysis to be achieved in practice, the orientation of the reactants would have to be controlled. We have been using a combination of theory and experiment to explore two alternative solutions to this problem. First, we have designed a surface model system to probe unfavourable Diels-Alder chemical reactions and coupled this to the break-junction technique in scanning tunnelling microscopy.<sup>2</sup> This technique allows us to detect chemical reaction events at the single molecule level, whilst delivering an oriented electrical field-stimulus across the approaching reactants. Second, we have instead addressed problem of orientation of the electric field by making use of appropriately placed charged functional groups to provide the electrostatic stabilization for solution-phase reactions.<sup>3</sup> In this way, the direction of the local field experienced by the reaction centre is fixed, and by associating the stabilization or destabilization with the protonation state of an acid or base group, it has the advantage of providing a convenient pH switch. In this talk our experimental and theoretical results will be presented and the broader prospects for electrostatic catalysis discussed.

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3. (a) G.Gryn'ova, D.L. Marshall, S.J. Blanksby and M. L. Coote *Nature Chem.* 2013, 5, 474-481.
(b) G. Gryn'ova and M.L. Coote *J. Am. Chem. Soc.* 2013, 135, 15392-15403. (c) M. Klinska, L. M. Smith, G. Gryn'ova M. G. Banwell and M. L. Coote, submitted.

# Descriptors of reactivity and selectivity in chemical reactions catalyzed by solids

Enrique Iglesia,

Theodore Vermeulen Professor in Chemical Engineering, College of Chemistry, University of California at Berkeley Berkeley, USA

The function of metal oxide surfaces as acid and redox catalysts is described here by combining kinetic and isotopic experiments, structural and surface characterization, and theoretical assessments of elementary steps and binding sites based on density functional Such strategies exploit oxide clusters of known structure and diverse theory (DFT). compositions and crystalline microporous materials that provide well-defined confining voids to develop rigorous descriptors of reactivity and selectivity. DFT-derived deprotonation energies (DPE) and the proton affinity of gaseous analogs of transition states combine to determine reactivity for a broad range of acid-catalyzed reactions. DPE values rigorously reflect the acid strength of oxides, but represent an incomplete descriptor of their catalytic reactivity, because interactions between organic moieties (e.g. intermediates, ion-pair transition states) and the solid acids depend on the ability of molecules and oxide surfaces to reorganize charge. This requires, in turn, that DPE values be separated into their covalent and ionic parts and that transition states for various reactions be classified in terms of their ability to recover a fraction of each DPE part upon formation of the relevant ion-pairs at transition states. Redox cycles that mediate oxidation reactions, with few exceptions, are limited by the rate of the elementary steps that reduce metal centers in oxides via C-H bond activations. These steps involve late transition states containing a nearly formed O-H bond, making Haddition energies (HAE) for metal oxides the relevant descriptor of reactivity, when properly averaged over all types of lattice oxygen atoms exposed. In acid and oxidation catalysis by oxides, these DFT-derived reactivity descriptors accurately describe measured rates and selectivities for diverse reactions. Such reciprocal benchmarking of theoretical methods and of mechanistic inferences from experiments requires the use of solids that preserve known structures during catalysis, as well as the interpretation of chemical reactivity data in terms of elementary steps and rates normalized by the number of active sites.

Coauthors: Prashant Deshlahra, William Knaeble, Robert Carr, Andrew Jones

## ON THE DETAILED MODELLING OF HIGH TEMPERATURE NANOPARTICLES SYNTHESIS

## Markus Kraft

Department of Chemical Engineering and Biotechnology, University of Cambridge, Cambridge, UK

New findings and models of high temperature nanoparticle synthesis and, in particular, particle formation and growth from gas phase precursors are presented. The model construction starts by identifying possible chemical species relevant to the synthesis and growth of nanoparticles. Subsequently, a detailed chemical mechanism is proposed. The chemical mechanism is then reduced and coupled to a stochastic particle system which describes the evolution of nanoparticles from clusters of molecules to aggregates of nano-size. In order to do this we use automated modelling techniques, advanced stochastic algorithms and statistical methods. The following systems will be discussed: silicon nanoparticle synthesis from silane, titania nanoparticles from titanium tetra-isopropoxide (TTIP) and titanium tetrachloride (TiCl4) and silica nanoparticles from of tetraethoxysilane (TEOS).

Lecture abstracts

Keynote lectures

## RECENT ADVANCES (AND CONTINUING CHALLENGES) IN COMBUSTION CHEMISTRY

William H. Green<sup>\*1</sup>, Shamel S. Merchant<sup>1</sup>, Aaron G. Vandeputte<sup>1</sup>, Connie W. Gao<sup>1</sup>, Nick M. Vandewiele<sup>1,2</sup>, Nathan W. Yee<sup>1</sup>, Marko R. Djokic<sup>2</sup>, Kevin M. Van Geem<sup>2</sup>, Guy B. Marin<sup>2</sup>

1) Department of Chemical Engineering, Massachusetts Institute of Technology Cambridge, MA, USA

2) Laboratory for Chemical Technology, UGent, Ghent, Belgium

#### Abstract

Combustion Chemistry is interesting and challenging because the chemistry can change significantly depending on the fuel, the reaction conditions, and the progress of the reaction. Under some reaction conditions, for example high-temperature ignition, or low-conversion pyrolysis, the chemistry appears to be well-understood, and we can generate quantitative predictive models for many fuels. As an example, we will show our recent results modeling JP-10 pyrolysis and combustion.<sup>1,2</sup> However, other chemistry such as low temperature ignition and soot formation is incompletely understood, and most existing models for these phenomena rely on empirical tweaks and/or unphysical irreversible or 'magic' reactions to get close to the experimental data. A variety of technical challenges which need to be overcome to make models predictive for any fuel will be reviewed. Obviously, in order to quantitatively model a phenomenon, it is very helpful to understand it in some detail. Here we report recent advances in understanding low temperature ignition, focusing on the various stages of the chemistry during stage 1 ignition. We also report an important advance in understanding how naphthalene and other 2-ring aromatics are formed from cyclopentadienyl ( $C_5H_5$ ) radicals.

#### Keywords

Low-temperature ignition, polycyclic aromatic, JP-10, predictive chemical kinetics, mechanism

### Introduction

Combustion is the major source of energy used by humans to provide electric power, heat, and transportation, so it plays a key role in the economy, and it is also the main source of local air pollution and greenhouse gas emissions. There is consequently a lot of interest in improving fuels and combustion technology to try to reduce the harmful effects of combustion systems, and to improve their efficiency and cost-effectiveness. Many important phenomena are sensitive to the kinetics of combustion chemistry, so ideally one would like to be able to rapidly construct accurate chemical kinetic models for any fuel in any combustion device under all operating conditions. Here we briefly review progress towards that goal.

Present methods seem to be working quite well for predicting many observables for simple fuels, but some of the most important observables are difficult to predict accurately. Here we focus in particularl on two critical challenges: predicting lowtemperature ignition delay, and predicting polycyclic aromatic formation (leading to soot). Ignition delay (measured as "octane" or "cetane") is a key performance metric for fuels in piston engines. In recent years it has become clear that human mortality and lifespan is strongly correlated with particulate levels in the atmosphere, and many of these healthharming particulates are soot formed by combustion.

Here we focus on three types of fuel: the C10 polycyclic synthetic jet fuel JP-10, n-alkanes, and simple alcohols. JP-10 ( $C_{10}H_{16}$ , *exo*-tetrahydro-dicyclopentadiene) is in particular an interesting test case for automated mechanism generation software, because of its tricyclic structure and because of the large production of cyclopentadiene as it decomposes, leading to questions about cyclopentadienyl radical kinetics. In particular there is considerable confusion in the literature about the recombination reaction of cyclopentadienyl radicals, which is found to result in formation of naphthalene ( $C_{10}H_8$ ) and H atoms. The reaction has been written [Murakami et al. 2003]:

$$C_5H_5 + C_5H_5 \rightarrow C_{10}H_8 + H + H \quad (Rxn \ 1)$$

which if correct implies the reaction accelerates the chemistry by converting unreactive  $C_5H_5$  into H.

The ignition delays of simple alcohols and nalkanes have been very well studied in the past; here we present a relatively simple way to understand their complicated pre-ignition chemistry, which proceeds through several phases each with different kinetics. • To whom all correspondence should be addressed

#### Methods

Kinetic models were expanded using the Reaction Mechanism Generator (RMG) software package [http://rmg.mit.edu], building on several seed mechanisms from the literature. Most of the thermochemical and rate parameters were estimated using functional group extrapolations from quantum chemistry calculations (typically CBS-QB3 or CCSD(T)-F12a//BMK/6-31G\*) or literature data on analogous species and reactions.

Pressure-dependent rate coefficients were computed by RMG, typically using the modified strong collision (MSC) approximation and other approximations detailed by [Allen et al. 2012]. The JP-10 high-temperature oxidation & pyrolysis model [Gao et al. 2015] was built starting from the detailed pyrolysis model of [Vandewiele et al. 20151 incorporating small-molecule reactions from GRI Mech 3.0 [Smith et al.]. The JP-10 model predictions were compared with measured product distributions from single-pulse shock tube experiments measured by Bonomi, Oluwole, Magoon, and Lewis [Gao et al. 2015]. For analysis of low-T ignition, we used the detailed propane model of [Merchant et al. 2015] and several n-alkane models from literature.[Healy et al. (2010); Mehl et al. (2011)] The quantum chemistry calculations on cyclopentadienyl + cyclopentadiene and cyclopentadienyl radical recombination discussed here were incorporated into a model generated by RMG and compared with Djokic's experiments on pyrolysis of cyclopentadiene [Djokic et al. 2014] and a mix with ethene; full details will be published separately [Vandeputte et al. 2015].

An important technical issue for JP-10 is how to accurately estimate the thermochemistry of the many fused-ring intermediates; simple methods for computing the thermochemistry of these species are not very accurate due primarily to mis-estimation of ringstrain and ring contributions to the entropy. Here, ring corrections for the most important species were mainly obtained from isodesmic reaction schemes using CBS-QB3, and other thermochemical and rate parameters for important species were computed at the BMK/6-31G\* level. Some of the potential unimolecular reactions of fused cyclics have a high degree of ring strain; here we assumed the rates of the high-strain pathways are negligible compared to the low-ring-strain competing routes, and so we omitted them.

#### Results

JP-10 model. RMG was used to construct a JP-10 high-temperature oxidation/pyrolysis model with 691 species and 15,518 reactions. In high temperature conditions (above about 1000 K) the chemistry is largely determined by how the radicals formed from H-

abstraction from the fuel decompose. Since JP-10 is tricyclic, the initial radical typically ring-opens before fragmenting, forming an intermediate fused-ring radical. Since several H-abstractions and  $\beta$ -scissions have comparable rates, there are more than a dozen significant competing decomposition pathways, Fig. 1.



Fig. 1. Some key pyrolysis pathways of JP-10

The model predictions are mostly in good agreement with the experimental data; a typical model prediction vs. data comparison is shown in Fig. 2



Fig.2. RMG model predictions (curves) and experimental single-pulse shock tube measurements (symbols) of cyclopentene yield from JP-10 partial oxidation (red  $\phi$ =0.14, orange  $\phi$ =0.24, green  $\phi$ =1) and pyrolysis (blue). Initial JP-10 mole fraction 0.2%, 7 atm Ar, t~0.5 ms. Typical experimental error bars shown on one data point.

While the results are highly encouraging (we have demonstrated we can predict many details of the chemistry of a real jet fuel at many different conditions *a priori*!), the process of constructing this model exposed several weaknesses of the current RMG software and databases (e.g. RMG uses too much RAM

and is rather slow; there are many holes and some mistakes in the databases).

*Cyclopentadienyl Recombination*. We (and others [Lindstedt & Rizos (2002)]) find that something must be wrong with the published stoichiometry and/or rate coefficient of Rxn 1: using the quoted rate coefficient the chemistry runs too fast, and makes too many H atoms. Our quantum chemistry calculations, which are largely consistent with prior calculations by Kislov & Mebel (2008), indicate that Rxn 1 is actually quite slow, so this competing 3-step reaction sequence dominates at ordinary pressures, temperatures and radical concentrations:

$$C_5H_5 \bullet + C_5H_5 \bullet = C_{10}H_{10}$$
 (Rxn 2)

where there are several partially-equilibrated  $C_{10}H_{10}$ isomers, which at ~1000 K live long enough to react bimolecularly (and exothermically) with almost any radical R• to form one of several  $C_5H_5$  substituted cyclopentadienyl radicals:

$$C_{10}H_{10} + R \bullet \rightarrow C_{10}H_9 \bullet + RH \qquad (Rxn 3)$$

The partially equilibrated  $C_{10}H_9$  radicals can then undergo a series of unimolecular isomerizations to form naphthalene:

$$C_{10}H_9 \bullet \rightarrow C_{10}H_8 + H \bullet \qquad (Rxn \ 4)$$

The rate-determining step in the isomerization sequence is opening of a  $C_{10}H_9$  intermediate with a 3-membered ring fused to a five-membered ring to form the first 6-membered ring; the second ring is formed in a similar way.

The sum of Rxn 2 + Rxn 3 + Rxn 4 is the overall reaction of this sequence:

$$C_5H_5 \bullet + C_5H_5 \bullet + R \bullet \rightarrow RH + C_{10}H_8 + H \bullet (Rxn 5)$$

So by this sequence three radicals are consumed to make one radical (the H atom), likely slowing down or the overall chemistry. This is very different from Rxn 1, where two unreactive cyclopentadienyl radicals are transformed into two much more reactive H atoms without any reduction in the number of free radicals. Replacing Rxn 1 with Rxns 2,3,4 brings our kinetic model into much closer agreement with cyclopentadiend pyrolysis and cyclopentadiene+ethene co-pyrolysis data measured at UGent.[Djokic et al. (2014), Vandeputte et al. (2015)] We find, both in the model and experimentally, that  $C_5H_5 + C_5H_5$  leads primarily to naphthalene formation, while  $C_5H_5 + C_5H_6$ leads primarily to indene formation; in many systems these are expected to provide fast routes to two-ring aromatics.

Understanding Low-T Ignition Delay. It has often been observed that some fuels exhibit "two-stage" ignition delays, where T(t) rises briefly then flattens out before rising again to very high temperature (the "hot ignition"). This is thought to be related to the phenomena of "negative temperature coefficient", where the ignition delay is a non-monotonic function of the temperature. Here we analyze the pre-ignition chemistry in detail, and discover that all fuels go through different phases in their chemistry.

In the initial phase, all the radical and product concentrations are very small, and the fuel and oxygen concentrations are nearly constant, so the kinetics are nearly linear, and the kinetic equations can be solved using eigenvalue techniques. Igniting systems typically have one positive eigenvalue, and the radical concentrations grow exponentially in a fixed proportion set by the corresponding eigenvector. The magnitude of the eigenvalue is related to the gain of the corresponding "chemical amplifier", the autocatalytic reaction cycle responsible. During this exponential phase, the concentration of radicals climbs by many orders of magnitude in a relatively short period of time.

Often HO<sub>2</sub> is the highest concentration radical during the exponential phase, and the linear-kinetics assumption typically fails when the HO<sub>2</sub> concentration grows so high that the reaction HO<sub>2</sub> + HO<sub>2</sub> becomes significant. When this happens, the growth in radical and product concentrations slows, and semilog plots of concentration versus time exhibit a "knee", Fig. 3. Although nominally HO<sub>2</sub> + HO<sub>2</sub> is a radical recombination reaction, its product H<sub>2</sub>O<sub>2</sub> is a radical initiator, so while this reaction slows the chemistry, the radical concentration typically continues to climb through the knee.



Fig. 3. Predicted mole fractions of  $HO_2$  (scaled by 10-5) and OH, and temperature (right axis) for adiabatic propane ignition (P=10 bar,  $\phi$ =1 in air, To=650 K). Note the knee between stage A and stage B, when  $HO_2$ +HO<sub>2</sub> becomes significant.

While HO<sub>2</sub> is often the highest-concentration free radical pre-ignition, OH is usually the radical consuming most of the fuel. At low temperatures ( $\sim$ 650 K) most alkanes have a high gain chemical amplifier

for OH radicals operating via the famous QOOH cycle making the chain branching agent ketohydroperoxide OQ'OOH. However, as the temperature increases the gain of the QOOH cycle drops, suffering losses due to side reactions, particularly the endothermic reaction ROO  $\rightarrow$  HO<sub>2</sub> + alkene. When the gain drops below one, the ketohydroperoxide concentration peaks and then decreases; this change in the chemistry causes the point of inflection in T(t) interpreted as the end of stage 1 ignition. As the QOOH cycle becomes less important, different cycles involving H<sub>2</sub>O<sub>2</sub> as the main chain branching agent take over, with some coupling between the H<sub>2</sub>O<sub>2</sub> and QOOH cycles. Analysis of the gain of these cycles provides a relatively simple model for very low-temperature ignition delay, and how it depends on the fuel structure, fuel concentration, and O<sub>2</sub> partial pressure. General formulas have been derived for the n-alkanes, and recent results on alcohols will also be presented.

#### Conclusions

In recent years there have been dramatic advances in our ability to predictively model combustion chemistry, so that now it is possible to build fairly accurate highly-detailed chemistry models for simple fuels even before any experimental data on the fuel has been measured. The key numbers in the model are coming from prior experiments on small radicals, quantum chemistry calculations on small molecule analogs, and functional group extrapolations from those values..

However, low-T ignition and soot-formation are often incorrectly predicted, and sometimes these predictions are even qualitatively incorrect.

Here we have presented some recent progress in understanding cyclopentadienyl chemistry leading towards soot formation, replacing the widely used (but in our opinion qualitatively incorrect) Rxn 1.

We also present an analysis/perspective on low-T ignition which focuses attention on the different phases of the chemistry, and on a few key reactions which control the chemical amplifier gain. We hope focusing attention on the most important aspects of this complicated chemistry will facilitate progress in understanding and ultimately predicting fuel performance in advanced engines *a priori*.

#### Acknowledgments

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## CLOUDFLAME AND PRIME: ACCELERATING COMBUSTION RESEARCH IN THE CLOUD

Zachary Reyno-Chiasson<sup>1</sup>, Naveena Nettyam<sup>1</sup>, Gokop L. Goteng<sup>1</sup>, Matthew Speight<sup>2</sup>, Bok Jik Lee<sup>1</sup>, Sathya Baskaran<sup>1</sup>, Jim Oreluk<sup>2</sup>, Aamir Farooq<sup>1</sup>, Hong G. Im<sup>1</sup>, Michael Frenklach<sup>2</sup>, S. Mani Sarathy<sup>1\*</sup>

<sup>1</sup> Clean Combustion Research Center, Division of Physical Sciences and Engineering, King Abdullah University of

Science and Technology (KAUST), Saudi Arabia

<sup>2</sup> Department of Mechanical Engineering, University of California, Berkeley, USA Corresponding authors: mani.sarathy@kaust.edu.sa; frenklach@berkeley.edu

#### Abstract

Research communities in kinetics and combustion utilize computational simulation applications to conduct effective and reliable studies. The Process Information Model (PriMe) [1,2] introduced a cyberinfrastructure for modeling and analysis of combustion kinetics, as well as data standards and workflows for linking simulation with data. In this research, the PrIMe infrastructure model is extended through the design and implementation of a platform-independent cyberinfrastructure. This model called CloudFlame consists of a joint cloud venture and an independently hosted cloud to provide open-source computational power, a digitized data warehouse, and a kinetics automation workflow for researchers. When employed by researchers at the Clean Combustion Research Center at King Abdullah University of Science & Technology and its collaborating partners the system resulted in significantly improved flexibility and portability of kinetics data and increased efficiency, scalability, and accessibility to computational resources. CloudFlame presents a new and exciting paradigm for collaboration in combustion and kinetics research that will enable future advances in computational chemistry, kinetic model development, experimental data management, uncertainty quantification, and reactive flow simulation.

Keywords

Low-temperature ignition, polycyclic aromatic, JP-10, predictive chemical kinetics, mechanism

#### Introduction

The term cyberinfrastructure (CI) was first introduced in the United States of America in the late 1990s as a technological security strategy aimed to protect critical information systems such as transportation lines, electricity grids, and banking systems. A well-known report published in the early 2000's by The National Science Foundation (NSF) reformed the concept of a CI as a tool for improved research and discoveries by integrating high performance computing, data, visualization tools, and scientific collaboration [3], [4]. This resulted in a modern, research-oriented definition of a cyberinfrastructure (CI) consisting of computational systems, data and information management, advanced instruments, visualization environments, and people, all linked together by software and advanced networks to improve scholarly productivity and enable knowledge breakthroughs and discoveries not otherwise possible.

Scientific fields that have successfully implemented CIs include environmental earth sciences for disaster management [5], [6]; chemical engineering for chemical process control [7]; biomedical sciences [8], [9], [10]; archeology [11]; social sciences [12], [13], [14], [15]; kinetics and combustion [1], [16], [17]; and computational sciences [18], [19]. These diverse scientific disciplines share the common objective of implementing CIs in order to enhance collaboration

and resource sharing among distributed researchers [20].

The benefits of CIs for research communities has been however the well documented, process of implementing a successful CI comes with a host of challenges. In the initial design stage, the logical and physical design of the systems involved must be identified to determine CI data flows, inputs, outputs, processing requirements, storage requirements, and user interfaces. When required aspects of a CI implementation are not reviewed prior to development. valuable resources and time can be wasted and this may result in CI implementation failures [21], [22]. Even in the case of a well-established design, the application of an effective CI can be difficult due to trade-offs between improved productivity and management complexity. For example, recent research projects have automated chemical workflow systems, improving productivity by reducing human time requirements, but have introduced complexity through complex data-flow structures [7] [23]. To address the issues of productivity and complexity in the present research, data-flow structures are as simple as possible while still reducing time required by researchers. Another common problem in CI implementation is the

reliability and security of distributed data shared across geospatial networks [25], [26], [27]. In order to balance accessibility and reliability of data, CloudFlame was implemented as a joint cloud consisting of a remote public component (Amazon Elastic Compute Cloud (EC2)) leveraging PriMe's data infrastructure and workflow and a locally hosted cloud running on King Abdulla University of Science and Technology (KAUST) servers. A cloud or cloud computing is a distributed computing system that provides scalable computational resources, data storage, databases, applications, visualization tools, sensors and instruments as services [33]. The publicly hosted cloud of CloudFlame can be remotely accessed via the PriMe web-portal using personal computers (PCs), laptops, or any hand-held device with an internet connection. All public data is verified and curated by experts, and placed into a catalogue of approved data for simulation workflow. This data verification is essential as the data-centric and data-driven nature of computational simulation [21] requires accurate generated results in order to make new and meaningful discoveries [28]. Additionally, certain shared data may contain sensitive or intellectual property information requiring restricted access. The locally hosted cloud is useful for sharing more sensitive data, utilizing a variety of security measures such as fire-wall restriction, encrypted communication using public/private keys, and remote connections via virtual private network (VPN).

Consistency across user platforms is maintained by PriMe and CloudFlame through the HDF5 binary data format for transporting data between clients and servers [2]. Intelligent cloud scripts written in Python and Bash convert HDF5 input files to the required format for simulation in software such as CHEMKIN-PRO [24] and Cantera [34], and generate HDF5 output for the client. Utilizing a common format of HDF5 provides many benefits such as fast transfer speeds of large files, consistency and quality of user data, and the flexibility to capture the complexity of a combustion model. Kinetic mechanisms, thermodynamic data files, and simulation boundary conditions can all be supplied within the format [2].

Research activities similar to that of PriMe and CloudFlame have been reported in the combustion In 1999, the Diesel Combustion community. Collaboratory (DCC) built a collaborative problemsolving environment for combustion experts [16]. DCC integrated combustion modelling, visualization, video conferencing, and data management capabilities. In 2001, the Soot Model Development Web Site (SMDWS) presented an implementation of internetbased collaborative infrastructure for combustion experts to share experimental and computational results for problem exploration and solution in combustion [29]. Due to the damaging environmental effect of soot formation, SMDWS became a useful internet-based collaboration workspace for experts to study its characteristics, share data, and run simulations. Despite the efforts of researchers to implement CIs for combustion studies, many researchers are not using these systems as they are unstable, and lack the robust data formats and workflow necessary to encourage formation of virtual organizations of collaborative CIs [30], [31].

In 2011 a community for building CI for combustion research was formed and charged with the responsibility of assessing the successes and failures of current combustion CIs [32]. During evaluation the committee came up with several suggestions for CI success such as implementation of a hierarchal method to combustion simulation, a workflows approach, and the planning and involvement of users throughout the implementation lifecycle. Many of the difficulties highlighted earlier were also identified by the committee.

Through CloudFlame and the CloudFlame/PriMe integration we have implemented cloud products with robust and flexible automation workflows that attempts to apply the committee's recommendations and overcome the many difficulties discussed. To ensure a more stable and robust system, CloudFlame's remote solution extents the well-established PriMe architecture to enhance the experience of current PriMe users with access to various well-developed simulation apps. The bulk of simulation features provided by CloudFlame are Cantera based. This was preferred as Cantera is an open-source solution that makes its original source code freely available and may be redistributed and modified. By using open-source software, no licensing costs or use limitations are required for the simulation features CloudFlame provides.

PriMe and CloudFlame Joint Architecture

Optimization of combustion efficiency and understanding the mechanism that prevents full energy utilization of fuels relies on detailed knowledge of the underlying physics and chemistry. These systems are generally complex enough that models have been used to explore the effect of different feed and reactor conditions and have been successful in optimizing fuel mixtures and combustion performance. However, these models are extremely complex and often controversial. The data, which parameterize the models and compared to model predictions, are themselves complex and often open to interpretation. Furthermore, the models are developed by multiple labs using different technologies. Keeping track of models, parameters, and data in an integrated framework has proven to be a necessity in the field of combustion. The initiative named PriMe (for Process Informatics Model) is aimed to fulfill this need. [1]

PriMe is a systems approach for developing predictive models of reactive-flow systems that is based on the paradigm of scientific collaboration. The primary goals of PriMe are collecting and curating data, validation the data and quantifying uncertainties, and seamlessly linking the data and applications. This approach enables comparison between data and models, allowing the assembly of data into predictive models with quantified uncertainties to meet specific end user requirements.

The current PriMe CI is comprised of three principle parts: Portal, Data Warehouse, and Workflow. All parts have reached the state of stable operation, and are functional [1]. The current PriMe CI was demonstrated to handle the laboratory combustion data collected in shock tubes and laminar prefixed flames, with the underlying data models and standards developed to handle all types of data in principle [1], [2].

The PriMe Portal operates as a client entry point for PriMe's web services, containing web pages for browsing PriMe data and links for downloading and running the local component software that connects to PriMe Workflow. The Portal is built on the Drupal open-source software, including the organic-group modules, and implements user authentication and permissions to ensure service security. There are currently over 400 registered users and over 20 specialized work groups.

The PriMe Data Warehouse is designed to represent the most current complete set(s) of data available in the field of combustion. It contains experimental data, on both complex systems and on elementary reactions. Molecular properties are determined from quantum chemical calculations, reaction rates obtained from quantum chemical calculations, reaction rates obtained from reaction-rate theories, and similar information. A direct, read-only access to this data collection is accessible to everybody. In order to keep data provenance, the submission of new data and the updating of existing data records is available only to PriMe members. The present collection contains over 100,000 XML (Extensible Markup Language) files, installed and managed on a WebDAV (Web Distributed Authoring and Versioning) compliant server.

The center piece of the PriMe infrastructure is the PriMe Workflow Application (PWA). It is an application that links users and automation of data flow, all via simple and easily extendable interfaces. The PWA directs the flow of data among workflow components, without actually moving all the data. The components can include data archives, datamanagement applications (e.g. search), simulation tools (e.g. shock-tube solver), and data-analysis applications (e.g. uncertainty quantification). This is enabled by the PWA passing an XML file containing the identification of the component, component instructions (and most importantly in the context of the present discussion) links to the data-interface files generated by previously executed components. These interface files are Hierarchical Data Files (HDF5 files) developed by the National Center for Supercomputing Applications (NCSA). HDF5 files are binary XML files, which represent the most compact and efficient way of transferring large data arrays. PWA components are operated via PriMe web services.

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Fig. 1. PriMe Workflow Application (PWA)

The PWA is built on cloud computing, utilizing the Amazon Web Services (AWS) and Elastic server technology (EC2). All operations are envisioned to run on remote servers, linked and synchronized by webservices. The practical implementation of the PWA is web-based and built on the Microsoft platform. The PWA is comprised of a downloadable client run module and a main module that is hosted on a dedicated server. It is a user-friendly drag-and-drop application that does not require any programming experience on the part of the user. The user can begin with a previously-saved workflow or create a new one, by selecting components from a set of predefined objects (see figure 1). Each object represents an operation; e.g., retrieving an experimental data set from the Data Warehouse, carrying out a simulation, or performing analysis of the generated results. The built PWA infrastructure allows users to share the project with other PriMe members, either by making the project public or by selecting specific PriMe collaborators. Furthermore, the PWA is built to enable code developers to contribute their own applications,

uploaded via a menu-driven user interface through either a web-based or remote-server configuration. It is this latter feature that is utilized in the present model for enabling CloudFlame features for PriMe users. Similar to PriMe, the CloudFlame server utilizes Amazon Web Services (AWS) and Elastic server technology (EC2). The server hosts a remote webapplication that interfaces with the PWS and assists in the transfer of the XML files used for component identification and instruction as well as the HDF5 data identified within these XMLs. Based on the contents of the files received by the remote application, various simulations can be run on the received data and once complete, a link to the data-interface files outputted from the execution is seamlessly passed to the next workflow component (e.g. in figure 1, the data would be passed to the display component hosted by PriMe). Currently, the CloudFlame server executes a Python script that determines from the XML which Cantera simulation to run (e.g. Plug Flow. Closed Homogeneous). The script subsequently calls subscripts that assist in converting the HDF5 format into CTML (unique XML schema format) input required by Cantera, running the simulation, and generating HDF5 output (utilizing the h5py python module). The combination of the remote application and these intelligent scripts allow for seamless integration with the PriMe architecture, and form the basis for a joint cloud solution (see figure 2).



Fig. 2. Data Flows of Joint Architecture

### **KAUST CloudFlame Architecture**

Building on the PriMe model, CloudFlame provides digitized species data in the form of tables (MySQL format) and XML as well as direct access to open-source simulation applications on a dedicated server hosted at KAUST. Currently CloudFlame hosts laboratory combustion data collected in shock tubes, flow reactors, jet stirred reactors, and rapid compression machines. All of CloudFlame's features are accessible via a Portal built on the Drupal opensource software, with read-only data access available to all, and data-modification and simulation execution available for registered users. There are currently over 40 registered users of CloudFlame. Digitized data in CloudFlame can be searched by species or author information, apparatus (e.g. flow reactor, shock tube), property (e.g. pressure, temperature), and property bounds, all within a simple web interface (see figure 3). The files can be downloaded in various user friendly formats such as CSV, XLS (excel), and PDF. Additionally, registered users can submit new data in the form of published results of experiments that are subject to validation process and eventual inclusion to the database.

•	جامعة الملك عبدالله للعلوم والتقنية King Abdullah University of Science and Technology	CloudFlame
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Fig. 3. Mechanism File Converter

CloudFlame hosts various Cantera Simulation scripts for executing ignition, flame speed, and counterflow diffusion flame calculations. CTML mechanism files that contain the necessary input for Cantera are available via a drop down for well-known mechanisms such as GRI-Mech 3.0, AramcoMech 1.3, and C1-C5 AlcoholMech. Additionally if a user wants to employ their own Cantera mechanism file they may upload it directly, or utilize the mechanism file converter to convert ChemKin files or HDF5 files to the proper format (see figure 4). The ability to preview the structure of various species of mechanisms is also available, and is useful for students and researchers to help identify compounds (see figure 5).

Navigation	Search Digitized Data
<ul> <li>Counterflow Diffusion Flame</li> <li>Flame Speed Calculation</li> <li>Ignition Simulation</li> </ul>	Choose Category* Species v
Calculation Mechanism File Converter	Choose Species *
Work Group	Choose Apparatus *
	Flow Reactor
	Choose property * Pressure V
	Enter Minimum Pressure Value *
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Fig. 4. Searching Digitized Data

All required parameters for running simulations are inputted via simple web forms built via Drupal and PHP (HTML-embedded scripting language). For example, a user running an ignition simulation can choose constant volume and/or constant pressure constraints, equivalence ratio, pressure, and temperature properties, as well as fuel composition and oxidizers. The simulation output generated by CloudFlame can be downloaded in CSV or HDF5 format, and graphs are also generated for researcher interpretation.

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Fig. 5. Species Structure Preview

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A recent feature has been the addition of work groups, to enable the sharing of files during collaborations (see figure 6). This was a proposed feature made by users of CloudFlame.

gation	Search Digitized Data
nterflow Diffusion ne ne Speed Calculation tion Simulation	Choose Category * Species v
ulation	Choose Species *
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k Group	Choose Apparatus *
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Fig. 6. Work Groups for Collaboration

### Analysis and Results

CloudFlame uses open-source software such as Drupal and Cantera, allowing unrestricted public usage and reducing implementation cost. Although this presents a significant benefit, open-source software my not be as reliable in providing accurate simulation results as commercial competitors such as ChemKin. In order to test this concern, simulations with identical input parameters were run on both software solutions. Flame speed calculations and ignition delay calculations were executed with various equivalence ratios (Phi) and the resulting velocities and times were recorded (see figures 7,8). Based on the results, Cantera provides accurate simulation data with a very small difference margin, with the ignition delay results being identical for Cantera and ChemKin. It was also found during testing that Cantera can solve various simulations with lean mixtures that ChemKin cannot, such was the case with an equivalence ratio of 0.4 for the flame speed calculations (see appendix).



Fig. 7. Flame Speed Calculation Results



Fig. 8. Ignition Delay Calculation Results

Researchers have commented that the implementation of Cantera with a user friendly GUI (graphical user interface) is very useful, as it is difficult for an end-user without prior knowledge of programming software such as Python to configure. Additionally, the ability to run simulations on a server without the installation of any software locally is a convenient, efficient, and streamlined method of modeling combustion reactions. The software is also a great teaching tool for students, and in previous versions of CloudFlame, decreased the human time required to run simulation calculations. In 2014, 10 students utilized the PriMe/CloudFlame workflow and the ChemKin software package to run identical simulations and found that the total user time required was 5-10% less when using the CloudFlame solution. At this time PriMe required the manual upload of mechanism files, whereas now they are stored in the Data Warehouse, thus the user required time has likely further decreased.

Although Cantera has provided accessible simulation solutions for CloudFlame it does have a few drawbacks when compared to commercial software. Due to the method of matrix solving in Cantera, the CPU (central processing unit) runtime of a simulation can be significantly longer than that of ChemKin, and can increase exponentially at low temperatures and at a high number of mechanism species. However, as Cantera is open-source we have the ability to modify the code and libraries used, and thus plan to provide performance upgrades in the future such as multithreading, GPU (graphics processing unit) utilization, and replacement of solving algorithm libraries. **Conclusions** 

Computer processing for analysis and simulation of complex experiments has become increasingly common in research practices for companies and educational institutions globally. Unfortunately, the full potential of technological advances on research efficiency and collaboration has yet to be realized. This is partially due to inconsistent data, tools, and code used by different scientific fields and sub-disciplines as well as a lack of effective and used tools for resource sharing and widelv collaboration. A Cyberinfrastructure (CI) such as CloudFlame, which is comprised of various software tools, resources, data housing, and shared resources can be implemented to greatly improve the positive affect of technology on current scientific investigation.

As outlined in the present research, the use of an integrated framework for models, parameters, and data has been demonstrated as a crucial tool in the field combustion. Through enhancing the previous implementation of PriMe and building a dedicated server, CloudFlame aims to provide the unique simulation and collaboration facilities required by combustion scientists globally. The involvement of distinguished researchers and students, along with the use of new formats (HDF5) and current open-source software (Drupal, Cantera), has helped to evolve CloudFlame into an effective integrated solution, with future involvement and development expected to result in new users, features, and recognition of the reliability and accessibility of CloudFlame.

#### Acknowledgments

Research of this nature which is about collaboration and building collaborating infrastructure cannot be accomplished by a single individual or organization. We wish to thank King Abdullah University of Science and Technology (KAUST) and Saudi Aramco's FUELCOM program for generously sponsoring this research. Research at the University of California Berkley was supported by the NSF Chemistry Division, Cyber-enabled Chemistry Grant No. CHE0535542, the Air Force Office of Scientific Research, Grant Nos. FAA9550-08-1-0003, FA9550-10-10459, and FA9550-12-1-0165.

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Lecture abstracts

lectures

# THERMAL DECOMPOSITION OF PENTADIENES: THE EFFECT OF RESONANCE STABILIZATION ON THE KINETICS

Isabelle Weber<sup>\*</sup>, Sabrina Syskowski and Matthias Olzmann Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT) Karlsruhe, Germany

Keywords

pentadienes, shock tube, H-ARAS

The rates of unimolecular bond fission reactions are correlated with the bond dissociation energies of the breaking bonds. The bond dissociation energies, in turn, are related to the stability of the radicals formed. In the case of unsaturated hydrocarbons, resonance stabilization of the radicals is particularly important.

We examine such effects by investigating the kinetics of C-H bond dissociation in  $C_5$  diolefins. We study 1,2-pentadiene, *trans*-1,3-pentadiene, and 1,4-pentadiene, which represent different resonantly stabilized structures with the same sum formula. Propene is studied as a reference case.

We performed shock tube experiments at temperatures between 1100 and 1800 K and pressures between 0.4 and 4.5 bar with argon as bath gas. Hydrogen atoms as a reaction product were detected with atomic resonance absorption spectroscopy (ARAS). The rate coefficients were determined from the measured concentration-time profiles, and their temperature dependence is parameterized. For propylene the results are in agreement with the literature values.

Our results show clear differences between the rate coefficients for the various  $C_5$  isomers. At a given temperature, the rate coefficients decrease in the order 1,2-pentadiene, 1,4-pentadiene, *trans*-1,3-pentadiene, and propene by about a factor of 5 each. We examine these differences, which are in line with estimated bond dissociation energies, and discuss structural effects and the role of competing isomerization reactions. Consequences for combustion modeling are elucidated.

## THE EFFECT OF ALCOHOL AND CARBONYL FUNCTIONAL GROUPS ON THE COMPETITION BETWEEN UNIMOLECULAR DECOMPOSITION AND ISOMERIZATION IN C1-C5 ALKOXY RADICALS

Enoch E. Dames,\* Shamel Merchant, William H. Green Massachusetts Institute of Technology, Department of Chemical Engineering Cambridge, MA 02139

#### Abstract

Presented here is an overview for the thermal unimolecular decomposition of a variety of alkoxy radicals ranging in size from C1-C5. Three classes of molecules are examined: alkoxy radicals with hydrocarbon backbones, those with alcohol functional groups, and those with carbonyl functional groups. The chosen species represent many of those found during the combustion of fossil fuels as well as bio-derived alternatives. Density functional theory calculations were benchmarked against higher level couple cluster calculations and used to explore the potential energy surfaces of various systems. Transition state theory was used to calculate high-pressure limit rate coefficients of all radical intermediates in the regimes relevant to atmospheric chemistry and combustion. We show that the assumption that alkoxy radicals quickly decompose via  $\beta$ -scission to aldehydes and other radicals is not valid for some of the alkoxy radicals investigated in this work. We further illustrate how intra-H migrations in larger alkoxy radicals with carbonyl and alcohol functional groups can dominate unimolecular decomposition under combustion and atmospheric relevant conditions. Finally, carbonyl groups can increase or decrease intra-H migration barriers depending on their location relative to the transferring H-atom.

#### Keywords

alternative fuels, alcohols, ketones, alkoxys, combustion kinetics

#### Introduction

Alkoxy radicals are formed during the combustion of nearly all oxygenated and hydrocarbon fuels. Under combustion conditions, these radicals may undergo unimolecular decomposition to an aldehyde and another radical species. Hippler and coworkers have extensively probed the temperature and pressure dependent kinetics of alkoxy decomposition for many systems.<sup>2,6,7,9</sup> From a computational approach, Somnitz and Zellner have investigated the decomposition of C2-C<sub>5</sub> alkoxy radicals.<sup>11,12</sup> However, this decomposition can compete with intramolecular H-migration reactions in some alkoxy systems. The importance of 1,5 Hmigrations in alkoxy radicals has been demonstrated in the past in a study of reactivity trends for methoxy through heptoxy alkoxy radicals with emphasis on the increased overall complexity in intermediate and product species inclusion of these H-migrations can have on detailed kinetic models under atmospheric conditions.3 Vereeken and Peeters, in а comprehensives computational studies on H-migrations for a wide variety of alkoxy radicals for the conditions of 1 atm and 250-350 K, have noted that H-shift reactions for some larger carbonyl substituted alkoxy radicals dominate all other channels.141315 Such reactions are largely missing from detailed combustion kinetic models relevant to both hydrocarbon and oxygenated fuels, where the formation of alkoxy radicals containing carbonyl and alcohol function groups is expected.

The objective of this work is to identify alkoxy radicals with H-migration pathways that can compete with unimolecular decomposition, while providing reliable corresponding high-pressure limit rate coefficients for combustion relevant temperatures. Thus, the high-pressure kinetics of the two aforementioned reaction types were determined using transition state theory (TST) for the species illustrated and defined in Figure 1.

#### Methodology

Molecular geometries, force constants, and energies for all species and saddle points were determined at the M08SO/MG3S level of theory, utilizing QChem 4.1.10 A computational grid with 75 radial points and 434 angular points per radial point was used in the calculations for all species. Frequencies were scaled by the recommended value of 0.985. Loose internal degrees of freedom for relevant adducts and transition states (i.e., hindered rotors (HRs)) were treated separately by performing relaxed potential energy scans about the bond defining the internal rotor; these calculations were performed in Gaussian 038 at the BMK /6-311+G(d,p) level of theory.<sup>3</sup> Reduced internal moments of inertia for all internal rotors were estimated at the I<sup>(2,3)</sup> level as defined be East and Radom.<sup>4</sup> CCSD(T)-F12a/cc-pVTZ-F12 calculations used to benchmark the M08SO/MG3S relative energies were computed using Molpro<sup>16</sup>. Cantherm<sup>1(p5)</sup> was used for all transition state theory calculations, which were

• To whom all correspondence should be addressed

performed in the regions of 300-2000 K. Eckart tunneling corrections were applied to all relevant reactions.<sup>5</sup> Intramolecular H-migration reactions studied in this work are given a reaction type notation corresponding to the nature of the transition state:

*ixy* where 
$$i = 5, 6, 7$$
;  $x, y = [p]$ rimary,  $[s]$ econdary,  $[t]$ ertiary

*i* in the above expression denotes whether or not the transistion state is a 5-, 6-, or 7-membered ring structure, while p,s, and *t* correspond to the carbon type from which a H-atom is being abstracted. The specific alcohol and aldehyde alkoxy radicals studied in this work are illustrated below in Figure 1.



Figure 1. Nomenclature and structure of alkoxyaldehyde and alkoxy-alcohol radical species studied in this work.

#### Results

Relative energies computed the at M08SO/MG3S level of theory are compared to higher level calculations for the intra-H migration in npropoxy, and illustrated in Figure 2. M08SO/MG3S relative energies are within 1.5 kcal/mol of the CCSD(T)-F12a/cc-pVTZ-F12 values, with average deviations far lower. The use of the CBS-OB3 model chemistry was explored as well. However, CBS-QB3 relative energies differ from the CCSD(T)-F12a/ccpVTZ-F12 values by up to 4 kcal/mol, illustrating the unreliability of this model chemistry for alkoxy radical kinetics. Thus, the M08SO/MG3S model chemistry was used to compute the relative energies of all other species in this work.

The influence of accounting for loose internal degrees of freedom as 1D hindered rotors compared to the rigid rotor harmonic oscillator treatment (RRHO) is illustrated below Figure 3 for *n*-butoxy and *n*-pentoxy. The difference in computed rates (RRHO vs 1D HR) can exceed one order of magnitude, illustrating the importance of properly including loose internal degrees of freedom. In *n*-pentoxy for instance, the reactant species has 4 internal modes corresponding to internal

rotations that were described as 1D HRs in the final TST derived rate coefficient. The influence of properly accounting for HRs is more evident for intra-H migrations than for  $\beta$ -scissions because all the internal rotors are 'tied up' in the transition state. In contrast, inclusion of 1D HRs does not have a large effect on  $\beta$ -scission reactions since internal rotors within the reactant and transition state do not noticeably change.



Figure 2. Zero Kelvin (zpe included) relative energy comparisons for select isomerization and elimination reactions in iso-pentoxy between varying levels of quantum chemistry theory.



Figure 3. M08SO/MG3S computed rate coefficients for the dominant unimolecular fates of n-butoxy (left) and n-pentoxy (right). Dashed lines: TST computed rates using the RRHO assumption for all internal degrees of freedom; solid lines: TST computed rates using the 1-D *HR* approximation as described in the text for the loose internal rotors; black and grey circles: intra-H migration/ $\beta$ -scission competitive crossover temperature without the with and 1-D HR approximation, respectively.

A variety of linear and branched pure alkoxy radicals were studied in this work but not discussed in detail here - in general, intra-H migration reactions do not compete with the  $\beta$ -scission pathways below 550 K and at the high pressure limit, as illustrated in Figure 4. However, this is not the case for some of the alcohol and aldehyde species studied here. As illustrated in Figure 5, the H-shift of S4C4 is faster than the  $\beta$ scission of *n*-butoxy producing formaldehyde and *n*- propyl (this reaction is used as a prototypical  $\beta$ -scission for alkoxy radicals, and accurately describes the  $\beta$ scission for alkoxys with functional groups 2 or more carbons from the oxygen radical). In general, alcohol functional groups do not offer the enhanced preference for intra-H migration; as shown in Figure 5 - none of the selected species exhibit crossover temperatures above 550 K, primarily because the OH group reduces H-shift barrier heights by up to 4 kcal/mol compared to 7 kcal/mol for some of the carbonyl alkoxy radicals.

Figure 6 also illustrates several reactions of alkoxys where the intra-H migration competes with  $\beta$ -scission above 500 K. In one case - for S5C5 - the 1,5 H-shift is favored over  $\beta$ -scission up to 800 K. The 0 K ZPE-corrected barrier height for this reaction is predicted to be only 3.3 kcal/mol due to the location of the carbonyl group in the radical species. Barrier heights for some of the reactions examined here are plotted in Figure 7, along with the transition state type.



Figure 4. High-pressure limit rate coefficients of alkoxy  $\beta$ -scission (solid lines) compared with select intra-H migration channels. circles: intra-H migration/ $\beta$ -scission competitive crossover temperature.



Figure 5. Rate coefficients of 1,5-H shifts for various C4 alcohol and aldehyde radical intermediates. Thick light blue line: rate coefficient for  $n-C_4H_9O = CH_2O + n-C_3H_7$ .



Figure 6. Rate coefficients of 1,5 and 1,6-H shifts for various C5 aldehyde radical intermediates. Thick light blue line: rate coefficient for  $n-C_4H_9O = CH_2O + n-C_3H_7$ .

As illustrated in Figure 7, the position of the carbonyl groups relative to the oxygen radical can increase or decrease the barrier height to H-shift. In general, the *sp2* hybridized C=O bond increases the overall ring strain energy in transition state for reactions that contain a more centrally located carbonyl group. However, for carbonyl group locations close to the oxygen radical (e.g., S1C5 S1C4, S4C4), H-migration barriers are lower than that for n-butoxy by up to 7 kcal/mol.



Barrier of H-shift

Figure 7. Barrier heights for intra-H migrations in various alcohol and aldehyde radical intermediates, computed at the M08SO/MG3S level of theory. Reaction barrier height (0K, ZPE included) and type indicated besides each species and defined in the text. n-butoxy is highlighted as a reference.

#### Conclusions

Three classes of molecules were examined in this work: alkoxy radicals with hydrocarbon backbones, those with alcohol functional groups, and those with carbonyl functional groups. Although alkoxy radicals with pure hydrocarbon backbones can take part in intra-H migration reactions, their decomposition to aldehydes and other radicals dominate above ~500 K. Likewise, alkoxy radicals with single alcohol functional groups do not have a significant effect on the overall rate of H-shifting for the molecules examined here. On the other hand, intra-H migrations for alkoxy radials with carbonyl groups are shown to be preferred over unimolecular decomposition up to 800 K for species S5C5 and S4C4.

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# DECOMPOSITION PATHWAYS OF IMPORTANT KETOHYDROPEROXIDE MOLECULES

Judit Zádor

Combustion Research Facility, Mailstop 9055, Sandia National Laboratories Livermore, California 94551-0969, United States

Keywords

low-temperature combustion, autoignition, unimolecular decomposition, automated search, master equation

Ketohydroperoxides (KHPs) are formed in low-temperature combustion systems when the "second"  $O_2$  molecule adds to a carbon-centered hydroperoxyalkyl (QOOH) radical, the adduct isomerizes, and finally eliminates an OH radical. There are typically several other possible bimolecular products in QOOH +  $O_2$  reactions, however, ketohydroperoxides are often the favored ones, because their formation is driven by the large exothermicity related to the formation of the carbonyl moiety.

KHPs can further decompose at elevated temperatures and pressures. In a simple  $\beta$ -scission process an OH and an alkoxy radical is likely to be formed, leading to two radicals, and thus chain branching. However, the recently proposed Korcek mechanism (Jalan et. al, JACS, 2013, 35, p. 11100) creates two closed shell singlets instead, decreasing the potential chain branching propensity of KHPs. The recent detailed study of Goldsmith et al. (Proc. Combust. Inst., 2015, 35, p. 283) established pressure and temperature dependent rate coefficients for the decomposition of a KHP, OCHCH<sub>2</sub>CH<sub>2</sub>OOH, and also studied the effect of chemical activation, i.e., the decomposition of initially hot KHP molecules.

In this work I determine the pressure and temperature dependent decomposition rate coefficients for a series of KHPs. The exploration of the possible pathways is conducted with the KinBot code, which enables the systematic investigation of likely pathways as well as the exploration of the conformational space. KinBot can discover pathways that were previously not thought of, or would be tedious to explore "by hand." For instance, analogous to the Korcek pathway (dashed arrows) one can imagine that the H atom adds to the carbonyl C atom (instead to the carbonyl O atom), and the outer hydroperoxyl O atom adds to the carbonyl O atom (red arrows). The trivial products in the Korcek mechanism are an acid next to a carbonyl molecule. KinBot finds both pathways. Moreover, KinBot also finds an interesting, although high-energy, zwitterionic structure with a trivalent O atom in these systems.



## EXPERIMENTAL STUDY OF 3-PENTANONE PYROLYSIS AND OXIDATION

M. Aghsaee<sup>\*</sup>, B. Shu, O. Welz, M. Fikri, and C. Schulz Institute for Combustion and Gas Dynamics – Reactive Fluids University of Duisburg-Essen, Duisburg, Germany

#### Abstract

Thermal decomposition and oxidation of 3-pentanone ( $C_5H_{10}O$ ) were investigated behind reflected shock waves with high-repetition-rate time-of-flight mass spectrometry (HRR-TOF-MS) for quasi-simultaneous time-resolved multi-species measurements. The experiments were carried out with 3-pentanone mole fractions of 0.3–1% at temperatures between 1200 and 1580 K and a pressure of ~1.7 bar. Concentration-time profiles of 3-pentanone, CO, and  $C_2H_4$  during pyrolysis of 3-pentanone and of 3-pentanone, CO,  $C_2H_4$  CO<sub>2</sub>,  $H_2O$ , and  $O_2$  during the oxidation were measured. These data complement experimental literature results and extend them for larger precursor concentrations. To separate the CO and  $C_2H_4$  peaks that both appear at nominal mass 28, we performed further experiments using partially deuterated 3-pentanone-2,2,4,4-d4. We performed additional shock-tube experiments using mid-IR quantum-cascade laser absorption for time-resolved CO detection. The measured CO mole fractions were compared with simulations based on 3 different literature chemical kinetics models for 3-pentanone pyrolysis and oxidation. Good agreement was found for the pyrolysis experiments, whereas in the oxidation experiments all 3 models underpredicted the CO concentration at longer times.

#### Keywords

Kinetics, 3-pentanone, biofuels, fluorescence tracers, shock tube, mass spectrometry, laser absorption.

#### Introduction

Amongst other ketones 3-pentanone (in the following, abbreviated as 3-P) has gained importance as a fluorescence tracer in combustion applications and as a component of next-generation biofuels. Tracers are used, e.g., for in-cylinder engine measurements to monitor quantities such as temperature, fuel concentration, and equivalence ratio using non-intrusive laser imaging techniques [1]. Ketones are frequently used as tracers because their fluorescence can be excited by common UV lasers [1] and the fluorescence can be detected without using specific UV transparent and sensitive equipment. The use of 3-P both as a bio-fuel component and as a tracer depends critically on the knowledge of its pyrolysis and oxidation kinetics.

Several chemical kinetics mechanisms were developed describing the oxidation and pyrolysis of 3-P [2-4]. These mechanisms were validated against, e.g., flame speeds, ignition delay times and time-resolved speciation data, the latter using laser absorption spectroscopy behind reflected shock waves.

In the present work we studied the pyrolysis and oxidation of 3-P behind reflected shock waves between 1200 and 1580 K and at pressure ~1.7 bar. The experimental results were then compared with kinetics models [2-4]. Shock tubes are widely used as versatile tools in gas-phase reaction kinetics studies of concentration-time profiles of numerous species with a fundamental time resolution of 10  $\mu$ s. Corresponding author:

#### mohammad.aghsaee@uni-due.de

In shock tubes, high-temperature reactions free of diffusion can be investigated at desired temperature and pressure conditions. For species detection, we used a high-repetition-rate time-of-flight mass spectrometry (HRR-TOF-MS) for quasi-simultaneous measurement.

#### **Experimental setup**

The experiments were conducted using two shock tubes with different instrumentation.

#### **HRR-TOF-MS** measurements

HRR-TOF-MS experiments were performed in a conventional stainless-steel diaphragm-type shock tube. Both the driver and driven section have an inner diameter of 80 mm. The driver section has a length of 2.5 m and the driven section measures 6.3 m. Aluminum sheets with thicknesses between 50 and 100 µm were used as diaphragms between driver and driven section. Helium was used as driver gas. A set of five pressure transducers (PCB-112A05) are positioned at equidistant distances of 150 mm between the transducer canters on top of the driven section of the shock tube. The fourth transducer is located 150 mm from the end plate. The fifth pressure transducer (PCB-112A05) was positioned at a distance of 20 mm from the end plate. Pressure and temperature behind the reflected shock wave  $(p_5 \text{ and } T_5)$  were calculated from shock-wave equations [5] using the initial pressure and temperature in the driven section  $(p_1 \text{ and } T_1)$  and the velocity of the incident shock wave. The latter was determined from the pressure transducer signals.

A precision manufactured conical nozzle (Frey) located in the center of the end flange separated the driven section and the mass spectrometer. All measurements presented here used a single 45  $\mu$ m nozzle only. The distance between the nozzle and the ion optics of the mass spectrometer was 8 mm to prevent Mach disc interferences [6, 7] and to achieve acceptable signal-tonoise ratio. All measurements were performed with electron impact ionization energy of 45 eV and in reflectron mode. Further details about the experimental setup and the data acquisition system can be found in [7]. Gas mixtures were prepared in a mixing vessel (50 1) and allowed to homogenize for 12 hours prior to use.

#### Shock tube for time-resolved CO measurement

Time-resolved CO measurements were performed in a shock tube with a length of driver and driven sections of 3 and 5.5 m, respectively, and an inner diameter of 8 cm. Two sapphire windows installed 20 mm upstream of the end wall were used for optical access. A continuous-wave quantum cascade laser (cw-QCL) housed with thermoelectric cooling (TEC) elements and collimating optics in a sealed laser housing (HHL housing) was used to probe time-resolved CO absorption by monitoring the P(20) line at 2059.91  $\text{cm}^{-1}$ . The operating wavelength of the laser was tuned by varying the input temperature and current, which were controlled by a TEC controller (Alpes Laser TCU 200) and a current controller (ILX Lightwave LDX-3232), respectively. Light emitted from the cw-QCL laser was focused into the center of the tube through a concave mirror (f = 20 cm) then collimated again by a second concave mirror with the same focal length placed symmetrically on the other side of shock tube. Afterwards, the laser beam passed through a beam-splitter (CaF<sub>2</sub>) to reduce the laser power to avoid saturation of the detector (VIGO PVI-3TE-5). A band pass filter  $(4.855 \ \mu\text{m} \pm 88 \ \text{nm})$  was installed in front of the detector to suppress unwanted emission from shock-heated gases. In this study direct absorption measurement with fixed wavelength was performed. To avoid any wavelength drift due to fluctuation of the ambient temperature the laser light was guided through an 8 cm long well-sealed stainless-steel cell filled with a CO/Ar mixture prior each shock-tube experiment to adjust the line position.

#### **Results and discussion**

#### Pyrolysis of 3-pentanone

The pyrolysis measurements were carried out with mixtures of 1% 3-P in Ne as the bath gas. 1% Argon was added as internal standard to correct all species intensities during the initial phase of the build-up of the molecular beam after the arrival of the shock wave. Hence, all species intensities are normalized to the Ar signal intensity. The oxidation experiments were performed with mixtures of 0.57% 3-P, 4% O<sub>2</sub>, and 1% Ar in Ne. Besides 3-P, product signal at mass-to-charge

ratio (m/z) = 28 (sum of C<sub>2</sub>H<sub>4</sub> and CO) was detected during the pyrolysis of 3-P. The resolution of the mass spectrometer does not allow distinguishing both species based on their exact mass, so that we can only report the summed signal intensity of C<sub>2</sub>H<sub>4</sub> and CO. To fill this gap, CO absorption measurements (see below) of 3-pentanone and additional HRR-TOF-MS experiments of partially detreated 3-pentanone (where CO and ethylene appear at different masses) were performed. The experimental data were compared with simulations based on a kinetics model of Serinyel et al. [2] and two models from the Stanford group [3, 4]. The first Stanford model [3] is based on the original model from Serinyel et al. [2] with some modifications in the main decomposition channels of 3-pentanone. In the updated model [4], a 3-P sub-mechanism consisting of 13 species and 61 reactions was developed where several reactions, like C<sub>2</sub>H<sub>5</sub>CO and C<sub>2</sub>H<sub>5</sub> decomposition, were changed to obtain better agreement with shock tube oxidation data. In order to compare our experimental data with the model predictions, the experimental time traces of C<sub>2</sub>H<sub>4</sub> and CO signal intensity were linked to absolute concentrations using the calibration factor of C<sub>2</sub>H<sub>4</sub>. Note that with the TOF parameters used in this study very similar calibration factors for C<sub>2</sub>H<sub>4</sub> and CO were found.



Figure 1: Time profiles for pyrolysis of 3-P at 1306 K and 1.65 bar. Red circles are 3-P and blue squares are  $CO+C_2H_4$ . Lines show the model results.



Figure 1 shows concentration-time profiles of 3-P and m/z = 28 for a pyrolysis experiment. The consumption of 3-P and the yield of C<sub>2</sub>H<sub>4</sub> + CO are well predicted by the model of Serinyel [2]. In contrast, the two Stan-

ford models [3, 4] yield a slightly more rapid consumption of 3-P and overpredict the yield of  $C_2H_4 + CO$ . With increasing the temperature, the agreement of the 3-P decomposition and CO production with the model of Serinyel gets even better, whereas the discrepancies with the models of Stanford remain.

#### Oxidation of 3-P

The oxidation experiments were performed with a stoichiometric mixture containing 0.57% 3-P, 4% O<sub>2</sub>, and 1% Ar in Ne. Besides 3-P,  $H_2O$ , m/z = 28 (CO + C<sub>2</sub>H<sub>4</sub>), O<sub>2</sub> and CO<sub>2</sub> were detected. Fig. 2 shows the concentration-time profile of m/z = 28 at 1350 K and 1.61 bar. Whereas the experimental trace is in reasonable agreement with the simulation based on the Serinyel model in the first 300  $\mu$ s, it is obvious that the peak in the CO concentration profile predicted by all three models is not resolved in our experiment. The red lines in Fig. 2 show simulated CO concentrations. The Stanford group also measured the CO concentration using laser absorption spectroscopy and they could resolve the peak in the CO concentration profile. Furthermore, C<sub>2</sub>H<sub>4</sub> is an intermediate (green lines), which according to the model is consumed after 400 µs, suggesting that the measured data after this time only represent CO. In addition, the models underpredict the experimental traces at longer time, a trend that becomes less pronounced with increasing temperature.



Figure 2: Concentration-time profiles of m/z = 28( $C_2H_4 + CO$ ) for 3-P oxidation at 1350 K and 1.61 bar. Symbols are measured CO +  $C_2H_4$ . Red and green lines show the simulations for CO and  $C_2H_4$ , respectively, based on the three models.

Figure 3 shows the time profile for  $CO_2$  for an oxidation experiment at 1350 K and 1.61 bar. The longer-time plateau in the  $CO_2$  concentration agrees well with the modeling results. However, the experimental induction time is not captured correctly by any of the models, and the experimental rate of formation is slower than the model predictions. With increasing the temperature, the induction time is well resolved by all models.

Figure 4 shows a concentration-time profile of  $H_2O$  for 3-P oxidation. All three models capture the longer-time plateau, whereas the Serinyel model predicts the rise of  $H_2O$  much better. With increasing the

temperature the difference between models is negligible and they are in an acceptable agreement with the measured data.



Figure 3: Time profiles of CO2 concentration from 3-P oxidation at 1350 K and 1.61 bar. Symbols are the experimental data. Lines show the model predictions.



Figure 4: Concentration-time profiles of H2O from 3-P oxidation at 1350 K and 1.61 bar. Symbols are the experimental data. Lines are the model results.

To distinguish between the contributing species at m/z = 28, we performed additional experiments with partially deuterated 3-pentanone-2,2,4,4-d4 (3-Pd4). This strategy allowed the separation of CO (m/z =28) and ethylene-d2 (m/z = 30) that would otherwise generate the same mass signal. Figure 5 shows the time profiles of C<sub>2</sub>H<sub>2</sub>D<sub>2</sub> and CO from 3-P-d4 oxidation at 1410 K and 1.48 bar. The sudden increase in the CO concentration and its subsequent rapid decay cannot be resolved in the measurements, which mask the CO shoulder despite isotope separation. In the calculation of the C<sub>2</sub>H<sub>2</sub>D<sub>2</sub> concentrations, the concentration was calculated based on the calibration factor of C<sub>2</sub>H<sub>4</sub>. This simplification, in addition to the fact that a kinetic deuterium isotope effect was not considered in the model might be the reason for the overprediction of  $C_2H_2D_2$  by all three models.



Figure 5: Concentration-time profiles of CO (black) and ethylene (red) from 3-P-d4 oxidation at 1410 K and 1.48 bar. Black triangles are CO and red circles are  $C_2H_2D_2$ . Lines show the prediction of the model results.

We additionally performed shock-tube experiments using mid-IR quantum cascade laser absorption as an independent time-resolved probe for CO. Figure 6 shows the measured CO profile for 3-P oxidation in comparison with simulations based on the Serinyel [2] and Stanford models [3, 4]. To link the absorbance to absolute concentrations it was necessary to account for the temperature dependence of the line strength when inferring the CO mole fraction profiles. As a first estimation, the temperature was taken from the model. In contrast to our HRR-TOF-MS experiments and in agreement with laser absorption experiments from the Sanford group, (performed at lower 3-P concentrations), our laser absorption experiments clearly show the peak-like shape in the time profile of CO, which furthermore agrees well with model predictions. As is the case for the HRR-TOF-MS results, all models underpredict the CO profiles at longer times. Further experiments are needed to clarify the reason for the absence of the CO peak in the HRR-TOF-MS data.



Figure 6: QCL absorption measurement of CO (red) from a 0.25% 3-P / 1.75% O<sub>2</sub> / Ar mixture at 1372 K and 1.2 bar and model predictions (black).

#### Conclusions

Pyrolysis and oxidation of 3-pentanone (3-P) was studied behind reflected shock waves with HRR-TOF-MS. The obtained experimental data were compared with

simulations based on chemical kinetics literature models for 3-P pyrolysis and oxidation. Measured results of 3-P pyrolysis were in a good agreement with model of Serinyel [2]. The concentration-time profiles of  $O_2$ , CO<sub>2</sub>, and H<sub>2</sub>O in oxidation of 3-P were measured and at increased temperature (T > 1450 K) there was a reasonable agreement between the experimental and model data. To separate the C<sub>2</sub>H<sub>4</sub> and CO peaks, which appear at the same mass, a series of experiments was performed with partially deuterated 3-P-2,2,4,4-d<sub>4</sub> and the C<sub>2</sub>H<sub>2</sub>D<sub>2</sub> concentration-time profile was in a good agreement with the simulation data. The peak in the CO concentration profile was resolved neither in 3-P oxidation nor in 3-P-d<sub>4</sub> oxidation in our HRR-TOF-MS experiments. We also performed additional shock-tube experiments with time-resolved CO detection. The sudden increase in the CO concentration-time profile was resolved but there is a discrepancy between the experiment and the simulations of all three models for CO at longer time, which is consistent with the HRR-TOF-MS experiments.

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## **INITIAL STAGES OF THE PYROLYSIS OF POLYETHYLENE**

Konstantin V. Popov, Vadim D. Knyazev\* Department of Chemistry, The Catholic University of America Washington, DC, USA

#### Abstract

An experimental study of the kinetics of the initial stages of the pyrolysis of high density polyethylene (PE) was performed. Quantitative yields of gas phase products and functional groups within the remaining polyethylene melt were obtained as functions of time (0 - 20 min) at five temperatures in the 400 - 440 °C range. Gas Chromatography and NMR were used to detect the products. A detailed chemical mechanism was created; rate constants of five critical elementary reactions were adjusted, resulting in an agreement between the model and the experiment. The values of adjusted rate constants are in general agreement with those of cognate reactions of small molecules in the gas phase, with the exception of the rate constants of the backbone C-C scission, which is found to be approximately one to two orders of magnitude lower. The dependence of the diffusion-limited rate constant of radical recombination on the changing molecular mass of polyethylene was explicitly quantified and included in the extended kinetic model, which appears critical for the agreement between modeling and experiment, particularly the agreement between the experimental and the calculated activation energies for product formation rates.

#### Keywords

Polyethylene pyrolysis, radicals, NMR, olefins, kinetics

#### Introduction

Combustion and flammability of polyethylene (PE) are important subjects of study directly related to such practical applications as fire safety and recycling of plastics. The process of pyrolysis is the initial step of combustion of the solid, with the gaseous products providing the fuel for the flame. Efforts have been directed onto elucidating of the details of the chemical mechanism of PE pyrolysis (e.g., Ranzi et al., 1997; Faravelli et al., 1999; Poutsma, 2003; Levine and Broadbelt, 2009). Nevertheless, the rates of the main elementary reactions that occur during pyrolysis and the roles of these reactions in the formation of the final products are still debatable due to the difficulty of experimental study of elementary reactions under the conditions of polymer melt. A very thorough review of the experimental and modeling studies of PE pyrolysis conducted by 2003 can be found in a review by Poutsma (Poutsma, 2003).

The current study focuses on the initial stages of polyethylene (high-density polyethylene, HDPE) pyrolysis, where only several types of elementary reactions are expected to play major roles, and secondary processes involving the products of the initial stages are negligible. A novel aspect of the experimental part of this work is in the use of two techniques to probe both the gaseous products and the abundances of specific functional groups in the remaining condensed phase (polymer melt that solidifies upon cooling). Nuclear Magnetic Resonance (NMR) spectroscopy was used to determine the kinetics of the formation of three types of carbon\* To whom all correspondence should be addressed carbon double bonds, terminal  $-CH_3$  groups, and chain branching points ( $CH_Y$ ) in the liquid polymer melt phase. Gas Chromatography (GC) was used to determine the yields of volatile products. Quantities of liquid phase and gas phase products were measured as a function of time (5 – 20 min) in the 400 – 440 °C temperature range. Experimental conditions were selected to limit the molar fraction of the formed double bonds in the condensed phase to less than 0.5% and thus isolate for study only the initial stages of the overall process.

The results were initially modeled with a short mechanism consisting of a limited number of reaction types: backbone C-C bond scission, beta-scission of alkyl radicals, hydrogen atom transfer via abstraction, addition of alkyl radicals to double bonds, and radical recombination. Steady state approximation was initially used to derive the relationships between the observable product yields and combination of rate constants of elementary reactions; analysis of the experimental data within the framework of the steady state model provided initial approximations for the rate constants of critical reactions. The steady state model was followed by modeling based on numerical integration of kinetic equations and the initial mechanism was expanded to include reactions of secondary importance, as well as the dependence of the diffusion-limited radical recombination rate on the average PE chain length. which undergoes modification during the pyrolysis. Modeling with the expanded mechanism was performed using integration of kinetic equations. The derived rate constant values were analyzed and compared with those of cognate reactions of small molecules in the gas phase.

#### Experimental

HDPE samples were pyrolyzed in airtight reactors in an atmosphere of nitrogen. Pyrolysis experiments were performed using previously degassed samples over the temperature range 400°C to 440°C; the time of pyrolysis varied from 5 min to 20 min. The gaseous products of HDPE pyrolysis were analyzed using Gas Chromatography (GC) and the condensed phase was analyzed using NMR. Both <sup>1</sup>H NMR and <sup>13</sup>C NMR were used for analyzing the condensed-phase fraction of the products of HDPE pyrolysis. Proton NMR spectroscopy was used to determine to determine concentrations of different types of double carboncarbon bond groups (vinyl, RHC=CH<sub>2</sub>,  $\delta = 4.8 - 5.1$ and 5.6 – 6.0; vinylene,  $R_1HC=CHR_2$ ,  $\delta = 5.2 - 5.6$ , and vinylidene,  $R_1R_2C=CH_2$ ,  $\delta = 4.7 - 4.8$ ) and  $-CH_3$ groups ( $\delta = 0.8 - 1.0$ ), whereas <sup>13</sup>C NMR was used to analyze for the -CH3 and CHY (PE chain branching points) groups.

The gas phase products quantified via GC analysis were alkanes and alkenes ranging in size from  $C_1$  to  $C_8$ . Generally, the growth of gas phase product abundances was linear with time. The largest abundances were those of  $C_3H_8$  and  $C_3H_6$ . The –CH<sub>3</sub>, CH<sub>Y</sub>, vinylene (VE), and vinylidene (VD) groups display linear growth with time; thus, the main quantitative characteristics of these species used in further analysis are their respective rates of production. The kinetics of vinyl groups (VL) is that of initial growth with a trend to saturation.



Figure 1. Symbols: experimental rates of formation of the  $-CH_3$  groups and ethylene as functions of

temperature. Lines: calculations obtained using the kinetic mechanism.



Figure 2. Experimental values of the molar fractions of vinyl groups as functions of time (symbols) and calculated [VL] vs time dependences obtained using the kinetic mechanism.

#### **Kinetic Modeling**

The analysis of experimental data was performed via kinetic modeling. At first, a short mechanism was created, which includes all the important reaction types, but at the same time is sufficiently simple to enable analysis via both the steady-state approximation and the integration of the differential kinetic equations. Then, the mechanism was extended to include other reactions, the importance of which is relatively minor compared to those in the short mechanism. The values and / or the ratios of rate constants were derived from fitting the calculated product formation rates and molar fraction profiles to the experimental data. Figure 1 - 4 display the results

of the calculations in comparison with the experimental data.



Figure 3. Symbols: (a) experimental average molar fraction of vinyl groups (VL, averages over the 5 - 20 min period) and (b) rate of formation of the vinylene groups as functions of temperature. Lines: calculations obtained using the kinetic mechanism.



Figure 4. Symbols: experimental rates of formation of vinylidene (VD) and  $CH_Y$  groups as functions of

temperature. Lines: calculations obtained using the kinetic mechanism.

41 reactions were included in the full mechanism. used for kinetic modeling. Here, reactants and products are denoted using terms emphasizing their functionality:  $-CH_2$ - is a single C-C link in the polymer chain,  $CH_Y$  stands for a branching site,  $CH_H$  is an Hlink, which forms by a recombination of two secondary radicals,  $R_P$  and  $R_S$  denote primary and secondary radicals, respectively. Rate constants for individual reactions are, again, described in terms of reaction types, e.g.,  $k_{\beta,S}$  is for the beta-scission of a secondary radical,  $k_{HT,SP}$  is for an H-atom transfer, i.e., abstraction by a secondary radical from a  $-CH_3$  group to form a primary radical,  $k_{AST}$  denotes addition of a secondary alkyl radical to a VL group in the terminal position, etc.

-CH <sub>2</sub> ·	$\rightarrow$	$2 R_P$		ks	(1)
$R_P$	$\rightarrow$	$C_2H_4$ -	- R <sub>P</sub>	$k_{\beta,P}$	(2)
$R_P  + $	-CH <sub>2</sub> -	$\rightarrow R_S +$	-CH <sub>3</sub>	k <sub>HT,PS</sub>	(3)
$R_S \ +$	-CH <sub>3</sub>	$\rightarrow R_P + \cdot$	-CH <sub>2</sub> -	k <sub>ht,sp</sub>	(4)
$R_S$	$\rightarrow$	VL + I	R <sub>P</sub>	$\mathbf{k}_{\beta,S}$	(5)
$R_S \ +$	VL	$\!$	CH <sub>Y</sub>	<b>k</b> AST	(6)
$R_S \ +$	Rs	$\rightarrow$	$CH_{\rm H}$	k <sub>RSS</sub>	(7)

Reactions 1 - 7 form the skeletal mechanism, sense that they largely determine the in a concentrations of the R<sub>P</sub> and the R<sub>S</sub> radicals and the yields of the main experimentally observable products: C<sub>2</sub>H<sub>4</sub>, VL, -CH<sub>3</sub>, and CH<sub>Y</sub>. Initiation (1) forms primary radicals, which can decompose via beta-scission to form ethylene and another primary radical (2) or abstract a hydrogen atom and thus form a secondary radical and a -CH<sub>3</sub> group (3). The secondary radicals can decompose to produce a vinyl group at the end of a long polymer chain (VL) and a primary radical (5) or revert to a primary radical via reaction 4 (the reverse of 3). VL groups can be destroyed by terminal or nonterminal addition of secondary radicals. Only terminal addition (6) is included here because the rate constant for non-terminal addition is expected to be significantly lower. Termination is described by the recombination of secondary radicals, Reaction 7. The rest of the reactions, including those responsible for the formation of VE and VD groups, are not listed here due to the lack of space.

The diffusion-limited rate constant for the radical recombination reactions ( $k_{RSS}$ ) was calculated using the Smoluchowski equation. The dependence of the rate constant on the PE chain length changing during the pyrolysis process was explicitly included in the model. Rate constants of the following elementary reactions were adjusted, using the steady state analysis equations as a guide: C-C backbone scission,  $k_S$ ; two kinds of H-atom transfer,  $k_{HT,PS}$  and  $k_{HT,SA}$  (abstraction of an allylic hydrogen); radical addition to the double bond,  $k_{AST}$ ; and beta-scission of tertiary alkyl radicals,  $k_{\beta,S}$ . The number of experimentally observable

quantities such as rates of product formation (7) exceeded that of adjustable parameters of the model (5).

The values of adjusted rate constants are in general agreement with those of cognate reactions of small molecules in the gas phase, with the exception of the rate constants of the backbone C-C scission, which is found to be approximately one to two orders of magnitude lower. This observation provides tentative support to the hypothesis that congested PE melt molecular environment impedes the tumbling motions of separating fragments in C-C bond scission, thus resulting in less "loose" transition state and lower rate constant values.

The current study is the first modeling work that we are aware of where the dependence of the radical recombination (kinetic chain termination) rate constant on the changing molecular mass of PE was explicitly quantified and included in a kinetic model. This inclusion resulted in significant improvement of the agreement between modeling and experiment. In particular, the phenomenological activation energies for the formation of major products decreased compared with the models where such dependence was not included; the calculated slopes of the temperature dependences of product rates of formation in Arrhenius coordinates became significantly closer to the experimental ones. Faster overall pyrolysis at higher temperatures means faster decrease in the average PE molar mass and thus faster increase in the rate of chain termination. The dependence of the kinetic chain termination rate constant on the changing PE chain length provides explanation of the previously experimentally observed phenomenon of initial fast pyrolysis followed by a slower stage.

One consequence of the effect of  $k_{RSS}$  decreasing during pyrolysis is that, for sufficiently long initial PE chains, the rates of appearance of major products eventually converge to the same values, regardless of the initial PE chain length. This is accompanied by the convergence of the time-dependent –CH<sub>3</sub> concentration and, thus, average PE molar mass,  $M_n$ . Figure 5 demonstrates predicted time dependences for –CH<sub>3</sub> and C<sub>2</sub>H<sub>4</sub> abundances and formation rates for hypothetical linear PE samples with the numbers of -CH<sub>2</sub>- groups N of 1000, 10000, and 100000 at 400 °C. The plots in Figure 5 demonstrate initial fast increase in pyrolysis rate followed by a relaxation to a lower value, with the same asymptotic behavior for the three samples of different molar masses.

#### Conclusions

An experimental study of the kinetics of the initial stages of the pyrolysis of high density polyethylene was performed. Quantitative yields of gas phase products and functional groups within the remaining polyethylene melt were obtained as functions of time (0 - 20 min) at five temperatures in the 400 - 440 °C range. Gas Chromatography and

NMR (<sup>1</sup>H and <sup>13</sup>C) were used to detect the gaseous and the condensed phase products, respectively.

A chemical kinetic mechanism of PE pyrolysis was created. Rate constants of critical elementary reactions were adjusted resulting in an agreement between the model and the experiment. The number of experimentally observable quantities such as rates of product formation (7) exceeded that of adjustable parameters of the model (5). The values of adjusted rate constants are in general agreement with those of cognate reactions of small molecules in the gas phase, with the exception of the rate constants of the backbone C-C scission, which is found to be approximately one to two orders of magnitude lower.

The results demonstrate the critical role of diffusion-controlled rates of kinetic chain termination in the overall kinetics of pyrolysis and the importance of the knowledge of the dependences of such rates on molar mass of PE and, potentially, its distribution, as well as other conditions.



Figure 4. Predicted time dependences for  $-CH_3$  and  $C_2H_4$  abundances and formation rates for hypothetical linear PE samples of different chain lengths at 400 °C. All three samples demonstrate the same asymptotic behavior for rates of product formation at long pyrolysis times.

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Simulation of Initial Product-Forming Pathways. *Macromolecules*, 24, 8931-8957.

### **Stochastic Kinetic Modelling of Polyethylene Pyrolysis**

E. Santos, A. Lemos, N. Trindade, M.A.N.D.A. Lemos, F. Lemos\*

CERENA, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

#### Abstract

A stochastic model was developed to describe the thermal and catalytic degradation of polyolefins, in particular of HDPE. The model is applied to information obtained in conventional thermal analysis experiments, using a simultaneous TG/DSC apparatus so as to obtain both the information on the weight change and the information pertaining to the heat involved in the various transformations. The model also allows the calculation of the product distribution obtained from this cracking process. In a previous version of this model we have assumed that the pyrolysis process proceeds by random C-C bond scission in the polymer; although the TG/DSC data is adequately described by this model, the product distribution was completely different from the experimental one. In this paper we analysed the influence of assuming different cracking probabilities for the C-C bonds, depending on their position in the molecule. Product distributions which are much closer to the experimentally obtained have been achieved.

#### Keywords

Polyethylene, pyrolysis, catalytic cracking, bond scission probability.

#### Introduction

Polyolefins are important oil-based commodities whose consumption increases rapidly (APME 2013) and, due to their chemical stability, their waste constitutes a significant environmental problem. Although recycling is the best option for this waste management, there is a large quantity of plastic that is not recyclable and for which thermal or catalytic degradation is a route to convert them to gaseous and liquid hydrocarbons (Marcilla et al., 2007a; Chaianansutcharit et al., 2007). Catalytic degradation has the advantage of reducing processing temperature and time and, thus, reducing the energy required for the production of hydrocarbon products (Coelho et al., 2012, Marcilla et al., 2007b, Pierella et al., 2005). In view of the complexity of the reactions involved a suitable model to understand and optimize the reaction is very important.

One of the difficulties that is encountered is the very large number of possible species, resulting in a very large number of differential equations to solve. These equations need to describe not only the kinetics but also the evaporation rate of each of the species involved.

The set of deterministic equations that would have to be solved would not only be very large but, most likely, stiff because of the widely different time constants associated with the different chemical and physical processes. Stochastic models are a suitable alternative for the solution of stiff problems (Gillespie, 2007), and have been applied to complex reaction systems (Ferm, 2010).

The purpose of this work is to contribute to the development of a stochastic model capable of describe a dynamic pyrolysis experiment carried-out in a simultaneous TG-DSC apparatus.

This model allows the computation of both the weight changes and the thermal fluxes involved, as well as estimating the composition of the products

In a previous work a first version of the stochastic model was developed assuming that random cracking occurred, i.e. the probability of cracking of a C-C bond was the same for all bonds (Trindade et al., 2014) but we found that product distribution was not adequately described. In this work we expand this model including non-uniform cracking probabilities.

#### Experimental

#### Plastic polymer, catalyst and other reagents

The reference data for the polymer degradation experiments were published elsewhere (Coelho et al., 2010) and correspond to the degradation of a pure HDPE sample supplied graciously by Repsol and the catalyst was a commercial ZSM-5 zeolite with a Si/Al molar ratio of 15 obtained in powder form from Zeolyst.

To calibrate the evaporation rate laws different hydrocarbons were used, purchase from chemical reagents suppliers. Evaporation experiments were carried-out using n-hexane, n-heptane, n-nonane, n-decane, n-dodecane and n-icosane.

To carry out these measurements a fixed amount of the reactant was place in the pan and the temperature was programmed as for a regular degradation experiment. Since only relatively light reactants were used, no significant thermal degradation was expected during these runs.

#### Thermogravimetric analyses

All DSC/TG experiments were carried out in a TA Instruments SDT 2960 simultaneous DSC-TGA apparatus. Prior to the experiments, the TG-DSC apparatus was calibrated according to the

<sup>•</sup> francisco.lemos@tecnico.ulisboa.pt

manufacturer's specifications, in relation to weight, temperature and DSC signals.

The test starts by equilibrating the sample at 40 °C for 10 min; the sample is then heated from 40 °C up to 600 °C at 10°C/min. The sample was then kept at 600 °C for 10 minutes and cooled down to room temperature. Unless otherwise specified all the experiments were carried-out under a continuous flow of nitrogen of 80 ml/min.

#### Computational model development

The computational model was developed in Visual Basic for Applications in Excel 2013. Although Excel imposes some constrains on the running speed of the computational model, it provides an extremely easy platform for data input and graphic generation. The programme computes the TG and DSC curves as well as the product distribution both overall and in the gasphase.

A more detailed description of the model can be found elsewhere (Trindade, 2014) but a brief summary follows below.

• bond breaking kinetics is first order in relation to breakable bonds (terminal bonds cannot be broken);

• evaporation kinetics is also first order.

The probability of occurrence of a first order processes in a given time interval is computed as

$$p_x = \frac{dx}{r} = kdt$$
 eq. 1

A bond vector is set-up so as to describe the molecular arrangement we wish to simulate, where each element stores a value that indicates if the bond is intact or broken and, in the case of the bond being intact if it is in the sample remaining in the pan or if it already in the gas phase.

A sequence of steps is repeated as the temperature is increased according to the experimental temperature programme. For each temperature the whole bond array is scanned and bond breaking and evaporation events are computed.

At the end the cycle, for each temperature, the mass remaining in the pan is computed, from which the contribution of the heat required for sample heating to the DSC is computed. The contribution of the energy involved in the bond breaking and evaporation are also computed. This allows us to obtain calculations of both the TG and the DSC signals. Product distribution is also computed as a function of time. The energy involved in the breaking of a bond is taken as independent of the bond position in the molecule and the heat of vaporization is fairly constant, independent of the size of the molecule.

All simulations were carried-out considering that each chain molecule had 10000 bonds. A fixed set of parameters – kinetic rate constants at a reference temperature, base activation energy (see below), heat capacity of the polymer, bond energy and vaporization enthalpy – was used.

#### **Results and discussion**

In order to develop the model, apart from the description of the reaction kinetics, the vaporization of the products has also to be computed. In the first part of this work a suitable vaporization law had to be developed, based on the vaporization experiments carried out in the TG/DSC apparatus with hydrocarbons of different chain length.

#### Hydrocarbon vaporization

The overall objective is to develop a general relationship that will allow the computation of the vaporization rates for compounds of arbitrary carbon chain length. Several empirical rate laws were tried (results not shown) and the best one was the use of a first order kinetic model for vaporization where the kinetic rate constant is computed according to the following relationships:

 $E_{av} \text{ (cal/mol)} = 8280.77+1512.05 n_b \quad \text{eq. 2a}$   $k_{vref} \text{ (min}^{-1}\text{)} = 440.14 \text{ e-}1.76 n_b \quad \text{eq. 2b}$ where  $n_b$  is the number of bonds in the hydrocarbon

molecule. Figure 1 depicts the fit for some of the vaporization experiments on pure compounds. After this procedure the model was also tested on mixtures of hydrocarbons (results not shown) with good results.



Figure 1. Vaporization curves of different hydrocarbons (from left to right  $- nC_6$ ,  $nC_7$ ,  $nC_9$ ,  $nC_{10}$ ,  $nC_{12}$  and  $nC_{20}$ ). Symbols - experimental data, lines computed using the stochastic model using the parameters indicated in the text.

#### Modelling

As a first attempt it was considered, as it is usually assumed in the literature (Aguado and Serrano, 1999) that the degradation process occurs by random scission of the bonds in the polymer. All bonds were considered as being breakable, except for the terminal bonds which would generate methyl radicals. Although some formation of methane can occur at high temperatures, since methane is a minor product in all cases, this assumption was taken as not very limiting.

Good fittings were obtained in relation to the mass curve and also to the DSC signal (Trindade, 2014) but the product distribution that was computed presented

an almost uniform distribution, which is not observed. Examples of the data obtained using this model are presented in Figure 2.

This led to the conclusion that, although the overall kinetics for bond breaking is adequate to estimate both TG and DSC, the assumption that random bond breaking with uniform probability for all bonds regardless of its position in the molecule is not adequate.



Figure 2. TG (a), DSC (b) and molar product distribution (c) computed using the stochastic model with uniform probability for bond breaking.

According to previous quantum-chemical calculations (Wang, 2001), it is likely that the activation energy for bond breaking is higher for bonds that are closer to the end of the carbon chain, as the carbocations or radicals are less stable.

To take this into account we considered that the activation energy for the bond breaking varies according to the relative position of the bond in question to the nearest chain end (n), according to the relation

$$E_{a_n} = E_a\left(\frac{ne+n}{n}\right) \qquad \text{eq. 3}$$

where  $E_a$  is the activation energy for the breaking of a bond very far from the edges and *ne* is the position of the bond for which the activation energy is doubled.

This generates a substantial difference in break probability of a bond as a function of the bond position in relation to the edge of the molecule, a difference that changes with temperature (see Figure 3 for an example). At lower temperatures this favours bond breaking away from the edge of the molecule but, as the temperature increases, the probability for bond breakings near the edge of the molecule increases faster than for inner bonds, which is in accordance with the fact that, experimentally, higher temperatures favour lighter product formation.



Figure 3. Relative (to n = 10) probability for bond breaking as a function of the distance to the edge of the molecule. Curves shown for ne=1.

As expected this changed considerably the product distribution, creating a maximum in the curve, as it is observed for actual product distributions, as it can be seen in Figure 4. This generates a distribution that presents a maximum, which occurs at increasing chain lengths as the value for *ne* increases, as it might be expected.



Figure 4. Molar product distribution computed with different values of ne.

The position of this maximum, however, occurs at carbon chain lengths that are significantly larger than the ones that are observed experimentally (Coelho, 2010, Coelho, 2012).

The increase of *ne* also induces changes in the mass and heat flow curves, shifting them to higher temperatures, as was to be expected, In fact the increase

in *ne* decreases the average kinetic rate constant for the breaking of the polymer C-C bonds and this decrease induces an increase in the temperature of degradation if the base kinetic rate constant is kept fixed. These results are depicted in Figure 5.



Figure 5. Influence of ne in the computed TG (a) and DSC (b) curves.

Notice that this decrease in the average rate constant, which induces the shift of the maximum of the heat flow associated with the reaction also reduces the overall of heat that is consumed by the reaction, consistent with the fact that products with higher molecular weights (fewer bond breaks) are produced.

#### Conclusions

The simulations that were carried-out indicate that, in order to explain the observed product distribution in the temperature programmed degradation of HDPE a non-uniform bond breaking probability has to be considered.

By considering the activation energy for bond breaking higher for bonds nearer the edge of the molecule, in view of the lower stabilization of the carbocations or radicals generated, the computed product distribution is much closer to the ones that are obtained experimentally.

Notice, however, that we have considered that all the reaction occurs inside the pan where the reaction is taking place; however, in particular at higher temperatures, it might be expected that some gas phase transformations could also occur that would also change the observed product distribution by decreasing the average molecular weight of the species that are collected. This aspects, however, is not considered to be very important because the residence time of the sample inside the oven in gas phase is relatively short. Further work is required to support the laws used to govern the change in reactivity of the different bonds.

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## **Global Uncertainty Analysis for RRKM/Master Equation Based Kinetic**

## **Predictions: A Case Study of Ethanol Decomposition**

Lili Xing,<sup>a,†</sup> Shuang Li,<sup>a,b†</sup> Zhaohui Wang,<sup>a</sup> Bin Yang,<sup>b</sup> Stephen J. Klippenstein,<sup>c</sup> Feng Zhang<sup>a,\*</sup>

<sup>a</sup>National Synchrotron Radiation Laboratory, University of Science and Technology of China, Anhui 230029, China

<sup>b</sup>Center for Combustion Energy and Department of Thermal Engineering, Tsinghua University, Beijing, 100084, China

°Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439, USA

*Abstract:* A precise understanding of the accuracy of reaction rate constants, whether determined experimentally or theoretically, is of considerable importance to kinetic modelers. While the uncertainties of experimentally measured rate constants are commonly provided, the "error bars" of computed (temperature- and pressure-dependent) rate constants are rarely evaluated rigorously. In this work, global uncertainty and sensitivity analysis is applied to the propagation of the uncertainties in the input parameters (e.g., barrier heights, frequencies and collisional energy transfer parameters) to those in the rate constants computed by the RRKM/master equation method for the decomposition of ethanol. This case study provides a systematic exploration of the effect of temperature and pressure on the parametric uncertainties in RRKM/master equation calculations for a prototypical single-well multiple-channel dissociation. Remarkably, the competition between dissociation and collisional excitation leads to uncertainties of more than a factor of 100 in the predictions for the higher energy channel. Overall, the present study illustrates the value of detailed qualitative and quantitative studies of the uncertainties in theoretical kinetics predictions.

Keywords: transition state theory, RRKM/master equation method, uncertainty analysis, sensitivity analysis, competition relationship

<sup>\*</sup> Corresponding author: feng2011@ustc.edu.cn

#### 1. Introduction

Unimolecular decompositions are commonly the first step in the conversion of a fuel in combustion systems. Correspondingly, the accurate determination of rate coefficients for unimolecular reactions has attracted a great deal of attention from combustion kinetics researchers.<sup>1-9</sup> The RRKM/master equation (ME) method is the preferred approach for computing the temperatureand pressure-dependent rate coefficients for unimolecular reactions.<sup>10-13</sup> The accuracy of RRKM/ME computed rate constants is highly dependent on the uncertainty of input parameters such as energy barriers, collisional energy transfer parameters, etc. Uncertainty estimates for such theoretical predictions are of crucial importance to combustion modelers because they propagate into uncertainties in the predictions for global observables such as the ignition delay and flame speed. Importantly, the uncertainties in such global observables provide an indication of the reliability of the model and are used to motivate further research into the reactions with the greatest contribution to the global uncertainties.

Recently, the random sampling high dimensional model representation (RS-HDMR) approach<sup>14-24</sup> was employed in a global uncertainty and sensitivity analysis of RRKM/ME rate constants for the oxidation of *n*-propyl radical by Goldsmith et al.<sup>25</sup> Enlightened by this prior work, we have employed the same RS-HDMR method to explore the temperature and pressure dependence of the uncertainties in RRKM/ME based kinetic predictions for the thermal decomposition of ethanol.

 $CH_{3}CH_{2}OH \rightarrow C_{2}H_{4} + H_{2}O$ (R1)  $CH_{3}CH_{2}OH \rightarrow CH_{3}+CH_{2}OH$ (R2)  $CH_{3}CH_{2}OH \rightarrow C_{2}H_{5}+OH$ (R3)

The simplicity of this reaction system allows us to directly explore the effect of this competition on the uncertainties in the predictions via the implementation of an extensive global uncertainty analysis for a variety of temperatures and pressures. Furthermore, the barrierless nature of (R2), leads to an interesting exploration of uncertainties arising from variational transition state theory (VTST) calculations. With the aid of sensitivity and uncertainty analysis for various temperatures and pressures, we will investigate these issues both qualitatively and quantitatively in this work.

#### 2. Theoretical methods

Only channels R1 and R2 were studied in this work since previous studies have shown that the C-O fission (R3) makes at most a minor contribution (<5%) under combustion conditions.<sup>26-28</sup>. For these channels, stationary point optimization and frequency analyses were performed with the B3LYP/6-311++G(d,p) density function method and single point energies (SPEs) were computed by QCISD(T)/CBS method based on calculations for the cc-pVTZ and cc-pVQZ basis sets.<sup>27, 29</sup> The dissociation curve for the barrierless channel R2 was constructed for a grid of C-C separations with a grid spacing of 0.1 Å using the CASPT2(2e,2o)/cc-pVDZ method and was then scaled by the ratio of the QCISD(T)/CBS<sup>27</sup> and CASPT2(2e,2o)/cc-pVDZ calculated dissociation energies. All the quantum chemical calculations were carried out with either the Gaussian 0930 or MOLPRO program packages.31 The C-C bond dissociation channel was studied with canonical variational transition state theory (CVT). The master equation simulations then couple these RRKM evaluations with models for the collision induced dissociation process in the determination of phenomenological rate constants for R1 and R2 at various temperatures and pressures. All the kinetic calculations were performed using the MESMER program.<sup>32-33</sup> Global uncertainty and sensitivity analysis were used to study the propagation of uncertainties in fundamental input parameters to those in the predicted temperature and pressure dependent rate constants.

Twenty two input parameters with specific uncertainties were chosen as the variables for the uncertainty and sensitivity analysis, as listed in Table 1. The uncertainties for these input parameters were chosen according to expert estimation for the current theoretical levels. The calculations were performed for temperatures ranging from 800-2000 K on a 100 K grid and for the five pressures of 0.001, 0.01, 0.1, 1, and 10 atm. The software GUI-HDMR<sup>34</sup> was used to perform this sensitivity and uncertainty analysis for reactions R1 and R2 based on the selected input parameters.

Table 1. The input parameters and their uncertainties used in the RS-HDMR analysis						
Parameters		Value (800 K)	Value (900-1200 K)	Value (1300-1800 K)	Value (1900-2000 K)	
1	C <sub>2</sub> H <sub>5</sub> OH	energy	0±1.0	0±1.0	0±1.0	0±1.0
2	CH <sub>3</sub> +CH <sub>2</sub> OH		85.6±1.0	85.6±1.0	85.6±1.0	85.6±1.0
3	C <sub>2</sub> H <sub>4</sub> +H <sub>2</sub>	20	9.7±1.0	9.7±1.0	9.7±1.0	9.7±1.0
4	TS2	energy	83.1±2.0	80.3±2.0	77.3±2.0	75.3±2.0
5	TS1	energy	66.0±2.0	66.0±2.0	66.0±2.0	66.0±2.0
6 C <sub>2</sub> H <sub>5</sub> OH		125±50%	125±50%	125±50%	125±50%	
7	C <sub>2</sub> H <sub>5</sub> OH		0.85±0.15	0.85±0.15	0.85±0.15	0.85±0.15
8	C <sub>2</sub> H <sub>5</sub> OH	L-J: σ	4.3±20%	4.3±20%	4.3±20%	4.3±20%

9	Ar L-J: σ (Å)	3.5±20%	3.5±20%	3.5±20%	3.5±20%
10	C <sub>2</sub> H <sub>5</sub> OH L-J: 8	450.2±20%	450.2±20%	450.2±20%	450.2±20%
11	Ar L-J: & (K)	113.5±20%	113.5±20%	113.5±20%	113.5±20%
12	C <sub>2</sub> H <sub>5</sub> OH	1.5±10%	1.5±10%	1.5±10%	1.5±10%
13	C <sub>2</sub> H <sub>5</sub> OH RRHO	272.9±10%	272.9±10%	272.9±10%	272.9±10%
14	C <sub>2</sub> H <sub>5</sub> OH RRHO	416.5±10%	416.5±10%	416.5±10%	416.5±10%
15	TS2 RRHO	83.7±10%	115.5±10%	142.7±10%	158.4±10%
16	TS2 RRHO	137.9±10%	204.9±10%	255.5±10%	281.7±10%
17	TS2 RRHO	184.5±10%	265.5±10%	342.6±10%	383.7±10%
18	TS2 RRHO	197.7±10%	275.2±10%	356.0±10%	399.5±10%
19	TS2 hindered	1.57±10%	1.64±10%	1.56±10%	1.60±10%
20	TS2 imaginary	123.0±20%	200.0±20%	246.8±20%	269.7±20%
21	TS1 RRHO	242.3±10%	242.3±10%	242.3±10%	242.3±10%
22	TS1 imaginary	1966.5±20%	1966.5±20%	1966.5±20%	1966.5±20%

#### 3. Results and discussion

The energy and uncertainty in the TS2 energy doesn't necessarily correlate directly with that of the corresponding dissociation energy; instead, it is also strongly dependent on the dissociation curve and the details of the VTST analysis. Figure 1 illustrates the C-C bond dissociation curves calculated at the CASPT2(2e,2o)/cc-pVDZ level and scaled to the QCISD(T)/CBS dissociation energy. The variation of the TS location with temperature is also shown in Fig. 1. The barrier height of the canonically optimized TS decreases with increasing temperature, which has a significant impact on the uncertainty analysis due to its effect on the competition between R1 and R2. It will be discussed in more detail below. The fact that the characteristics of the TS only change with temperature facilitates the uncertainty analysis. The key conclusions obtained from the uncertainty analysis are independent of whether the "transition state" for the barrierless reaction is analyzed by CVT or by VRC-TST



Figure 1. Calculated minimum energy pathway for the decomposition channel R2 ( $C_2H_5OH$ -> $CH_3$  +  $CH_2OH$ ) 3.1 Sensitivity analysis

Figures 2 and 3 show the variation of the sensitivities with temperature and pressure for R1 and R2, respectively. Large sensitivities to the energies of the reactant (C<sub>2</sub>H<sub>5</sub>OH) and transition states (TS) are observed for both reactions. Besides these energy parameters, the  $<\Delta E >$  down parameter [(125 $\pm$ 50%)(T/298)(0.85 $\pm$ 0.15) cm-1] is also seen to have a great influence on both k1 and k2 at the studied temperatures and pressures. The large uncertainty of the pre-factor of  $\langle \Delta E \rangle$  down ( $\pm 50\%$ ) contributes to the significance of its sensitivity factor. The other parameters, such as the imaginary frequencies and L-J parameters play minor roles. The slight irregularities in the sensitivity curves shown in Fig. 3 can be explained by the steps in the location of the canonically determined variational barrier, as shown in Fig. 1. The effect of the collisional energy transfer sigma) becomes parameters  $(<\Delta E > down,$ more significant with increasing temperature and decreasing pressure. This finding can be attributed to the fact that collision energy transfer and microcanonical dissociation rates become more competitive as the temperature increases and/or the pressure decreases. Interestingly, for k2, in addition to the expected large sensitivity to  $<\Delta E$ >down and the TS2 energy, there is also a strong sensitivity to the TS1 energy, while the sensitivity to the reactant energy is only of significance at high pressures. These findings are an indication that the population of states at energies near TS2 is greatly influenced by the rates for the dominant channel R1, especially at low pressure.

#### **3.2 Uncertainty analysis**

Figure 4 illustrates the variation in the overall uncertainty factors for k1 and k2 with temperature and pressure. In general, the uncertainties of both k1 and k2 increase with decreasing pressure, due to the uncertainties introduced by the collisional model and the interaction between collisional energy transfer and chemical reaction. The impact of pressure and temperature on the uncertainty of k2 is much greater than that for k1, because of the competition between collisional activation and dissociation for energies in the energy gap between TS1 and TS2. The apparent irregularities in temperature



**Figure 2.** The most significant first-order sensitivities for  $k_1$  (CH<sub>3</sub>CH<sub>2</sub>OH  $\rightarrow$  C<sub>2</sub>H<sub>4</sub> + H<sub>2</sub>O)



**Figure 3.** The most significant first order sensitivities for  $k_2$  (CH<sub>3</sub>CH<sub>2</sub>OH  $\rightarrow$  CH<sub>3</sub> + CH<sub>2</sub>OH)

behavior for the uncertainty of k2 at temperatures of 900, 1300, and 1900 K, can be explained by the presence of steps in the canonical variational TS location, which correlate with steps in the energy difference between TS1 and TS2. This change in the variational barrier height for TS2 affects the competition between the two channels and the collisional activation process, and consequently affects the uncertainties of k2. A physical consideration of the competition between collisional activation and dissociation helps explain the observed temperature and pressure dependence for the uncertainty in  $k_2$ . In a word, the HDMR method provides a great tool for investigating the propagation of uncertainty through RRKM/ME calculations, and the present calculations demonstrate that one should consider carefully the uncertainty in theoretical kinetics predictions for reactions with competing channels.



Figure 4. The natural logarithm of the uncertainty factors for  $k_1$  and  $k_2$ 

#### 4. Conclusions

The propagation of uncertainty during RRKM/ME calculations was studied using the ethanol decomposition as a case study. According to the sensitivity analysis, the energy transfer parameter ( $\langle \Delta E \rangle_{down}$ ), and the reactant and transition state energies have the largest contributions to the uncertainty of the rate constants for both channels. The difference in the sensitivity factors for the two channels is determined by the competition between collisional activation and dissociation. The computed rate constants have very similar uncertainty factors for the two reactions in the high pressure limit. These HPL uncertainties are controlled by the reactant and TS energies for the case of ethanol decomposition. At falloff pressure conditions, the uncertainties in the rate constants for C-C bond fission are related to the uncertainties in the collisional energy transfer parameters and more importantly by the energy gap between the two transition states.

Note

† Lili Xing and Shuang Li contributed equally to this work.

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# SPIN INVERSION AND SPIN SELECTION IN THE REACTIONS Fe<sup>+</sup> + N<sub>2</sub>O AND FeO<sup>+</sup> + H<sub>2</sub>

J.Troe\*, S.G.Ard, N.S.Shuman, V.G.Ushakov and A.A.Viggiano

University of Göttingen and Air Force Research Laboratory, Kirtland AFB

Keywords: Elementary gas phase reactions, statistical rate theories, ionmolecule reactions

Transition metal and transition metal oxide cations are known to react following the Two-State Reactivity concept, according to which high energy barriers in the reaction complexes can be avoided by spin inversion to excited electronic states with lower barriers. The properties of the rate constants of such reactions are shown to be fully representable by energy- and angular momentum-specific statistical rate theories. Examples are the reactions of FeO<sup>+</sup> with H<sub>2</sub>, CH<sub>4</sub> and CO and of Fe<sup>+</sup> with N<sub>2</sub>O (see refs 1-4). This talk reports recent work on the reactions of FeO<sup>+</sup> with N<sub>2</sub>O (or CO) and of Fe<sup>+</sup> with H<sub>2</sub>. The different reactivities of Fe<sup>+</sup> and FeO<sup>+</sup> as well as of sextet electronic ground state Fe<sup>+</sup> and quartet excited electronic state Fe<sup>+</sup> are rationalized.

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# RATE CALCULATION RULES FOR AUTOMATED GENERATION OF DETAILED KINETIC MODELS FOR HETEROCYCLIC COMPOUNDS

Fariba Seyedzadeh Khanshan\* and Richard H. West Northeastern University Boston, MA 02115

Keywords

Rate calculation rules, detailed kinetic modeling, heterocyclic compounds.

This is a theoretical study of the gas-phase unimolecular thermal decomposition of heterocyclic compounds via single step exo and endo ring-opening tautomerization reactions. However, the number of possible reactions in each reaction class is massive, and applying high-level electronic structure calculations for each would be prohibitively expensive. Instead, quatum chemical clculations were performed for a smaller set of reactions belonging to these two reaction classes, and data were used to derive rate estimation rules. Since the rate estimates are based on the local structure of the reacting sites, the effect of the ring size, hetoratom type, and attached functional groups were investigated. The calculations were performed for four, five, six, and seven membered rings including carbon, nitrogen, and oxygen heteroatoms. Results show that rate calculation rules are promissing for these single step ring-opening reaction classes. Further, results are compared with two-step ring opening reactions via diradical intermediates, and it is observed that the single step tautomerization reactions have lower barriers.

In order to study the effect of these direct ring-opening reactions in the automated detailed kinetic model generation, Reaction Mechanism Generator  $(RMG)^1$  has been used to build a predictive detailed kinetic model production of syngas from bio-oil gasification. Two models, before and after updating RMG's kinetic database with endo and exo tautomerization reaction classes, are built and compared. Since products from primary ring-opening reactions through C-O bond breaking are major contributors to CO and CO<sub>2</sub> formation, there are significant differences in syngas production between the two RMG-built models, demonstrating the importance of these reaction classes and their kinetic features when studying the thermal conversion of bio-oil.

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# COLLISIONAL ENERGY TRANSFER DURING COMPLEX REACTIONS IN MULTI-COMPONENT MIXTURES

Michael P. Burke Columbia University New York, NY 10027 mpburke@columbia.edu

Complex (or "pressure-dependent") reactions involve competition between simultaneous reactive and collisional energy transfer processes that depend on the surrounding gas mixture. In contrast to many laboratory conditions, most mixtures of practical relevance are comprised of multiple components, introducing potential for both bimolecular reactions involving the rovibrationally excited intermediate and complications in the energy transfer characteristics of the mixture. While the influence of bimolecular reactions of rovibrationally excited intermediates has been the subject of substantial recent attention in atmospheric (e.g. [1-4]) and combustion (e.g. [5]) environments, the influence of disparate collisional energy transfer characteristics in multi-component mixtures will serve as the primary focus here.

Significant fractions of species with disparate collisional energy transfer characteristics are relatively typical in combustion environments, where fuel, oxygen, intermediates, carbon dioxide, and water often reach mole fractions on the order of a percent to tens of percent. With the exception of oxygen, most of these other species are much stronger colliders than the main diluent (usually nitrogen). "Interaction" effects in multi-component mixtures for single-channel, single-well reactions are known to be exhibit rich behavior for mixtures of strong and weak colliders, where even low-pressure limit behavior has been shown to be more complicated than a simple summation of the contributions from individual components in isolation (e.g. [6,7]). Interaction effects for multi-well, multi-channel reactions are expected to be yet richer given the additional competitive processes involved.

Here, master equation calculations using the PAPER code [8,9] will be presented for various prototypical single-well, single-channel and multi-well, multi-channel reactions in multi-component mixtures to identify the controlling features of these interaction effects in a range of reaction types. Comparisons against various common rate coefficient representations will be shown to understand their limitations and explore opportunities for improved representations. Implications of these effects for various combustion predictions will also be demonstrated.

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# Theoretical challenges in oxidation chemistry of medium-sized molecules

Ewa Papajak<sup>\*</sup> and Judit Zádor

Combustion Research Facility, Mailstop 9055, Sandia National Laboratories, Livermore, California 94551-0969, United StatesLivermore, CA 94550

Keywords

Theoretical kinetics, master equation, anharmonicity

With the continuing need to understand oxidation chemistry in the troposphere and of the components of current and potential fuels, computational research is invaluable in obtaining quantitative description of the relevant chemical reactions. However, statistical thermodynamics and kinetics face several challenges in translating the *ab initio* molecular properties into rate coefficients and reaction mechanisms for the plethora of chemical reactions involved in atmospheric and combustion processes. In this study, we investigate and compare the computational cost vs. gain in accuracy from most prevalent methods used for two aspects of these calculations.

A large computational cost of electronic structure calculations of energy and vibrational frequencies for medium- and large-sized molecules is a well-recognized aspect affecting accuracy of rate coefficients. Another difficult task is proper accounting for the large amplitude motions in molecules to calculate partition function and density of states. The common practice is to apply harmonic oscillator approximation for the high-frequency vibrations and 1-dimensional hindered rotor approximation for the separable low frequency modes that correspond to the internal rotations along single bonds. However, for molecules with multiple coupled rotors, this approach cannot be applied and multidimensional treatments need to be employed.

In this work, we investigated the impact of multidimensional treatments on the accuracy of the pressure-dependent rate constants. <sup>1,2</sup> We discuss the balance of accuracy vs. computational cost between the electronic structure method and statistical mechanics treatment as it depends on the size of the system.

<sup>&</sup>lt;sup>1</sup> The role of anharmonicity and electronic structure theory accuracy in the theoretical prediction of the isobutane +  $O_2$  kinetics, Ewa Papajak and Judit Zádor, *in preparation* 

<sup>&</sup>lt;sup>2</sup> Direct observation and kinetics of a hydroperoxyalkyl radical (QOOH) John D. Savee, Ewa Papajak, Brandon Rotavera, Haifeng Huang, Arkke J. Eskola, Oliver Welz, Leonid Sheps, Craig A. Taatjes, Judit Zádor, and David L. Osborn, *Science* **347**, 643-646 (2015)

# EXPERIMENTAL INVESTIGATION OF THE OXIDATION OF DIMETHYL ETHER IN A JET-STIRRED REACTOR WITH PTR-TOF-MS, GC AND CRDS DIAGNOSTIC

Michael K. M. Ward<sup>\*1</sup>, Anne Rodriguez<sup>2</sup>, Olivier Herbinet<sup>2</sup>, Coralie Schoemaecker<sup>1</sup>, Fréderique Battin-Leclerc<sup>2</sup>, Christa Fittschen<sup>1</sup> <sup>1</sup>CNRS-Université de Lille – Villeneuve d'Ascq F-59655 Villeneuve d'Ascq, France <sup>2</sup>CNRS-Université de Lorraine 1 – Nancy F-54000 Nancy, France

Keywords

Low temperature combustion, jet-stirred reactor, PTR-TOF-MS, cw-CRDS

Due to current issues concerning the growing primary energy demand, not to mention a general interest in sustainable develpment, bio-fuels have become very promising in recent years. They are subject to extended research for the characterization of their reactivity and pollutant emissions. Dimethyl ether (DME) has attracted strong interest in the field of combustion: the simplest ether has a high cetane value (55-50) and a low toxicity together with significant decreases in the formation of soot particles and NOx [1]. Therefore, this molecule has been suggested as a possible additive agent or an alternative to diesel fuel.

Several experimental and theoretical studies have already investigated the combustion of DME under different conditions, using various equipments (jet-stirred reactor, shock-tube, counterflow diffusion flame, variable-pressure flow reactor) [2]. Even if they bring essential information, they were unable to establish a single model valid for all conditions. The objective of this study was to re-investigate DME oxidation with a different approach in order to complete existing experimental data sets, and subsequently better understand its reaction chemistry. Experiments have been carried out in a jet-stirred reactor operating at 800 Torr and 500-1100 K, and at different equivalence ratios: 0.25, 1 and 2. Reaction products have been analyzed using three complementary methods: Proton Transfer Time of Flight Mass Spectroscopy (PTR-TOF-MS), cavity ring-down spectroscopy (CRDS) and gas chromatography (GC).

The results will be presented, together with an improved kinetic model derived from these measurements.

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# A NOVEL WAY TO MEASURE SURFACE COMPOSITION OF SOLID MATERIALS BY HETEROGENEOUS TITRATION USING REACTIVE PROBE GASES

Elena Maters<sup>1</sup>, Araceli Tapia<sup>2</sup>, Pierre Delmelle<sup>1</sup>, Sagrario Salgado-Muñoz<sup>2</sup> and Michel J. Rossi<sup>3</sup>\* <sup>1</sup>Université Catholique de Louvain (UCL), Earth and Life Institute (ELI), BE-1348 Louvain-la-Neuve, Belgium <sup>2</sup>Universidad de Castilla La Mancha (UCLM), Departamento de Quimica Fisica, E-13071 Ciudad Real, Spain <sup>3</sup>Paul Scherrer Institute (PSI), Laboratorium für Atmosphärenchemie (LAC), CH-5232 Villigen PSI, Switzerland

#### Abstract

In order to characterize the surface reactivity of nanoparticles in terms of the number of surface functional groups a titration method based on six probe gases has been conceived in which heterogeneous gas-surface chemistry is used to "interrogate" the nanoparticle surface with which the probe gas kinetically interacts. The probe gases used were trimethylamine (N(CH<sub>3</sub>)<sub>3</sub>), hydroxylamine (NH<sub>2</sub>OH), hydrochloric acid (HCl), trifluoroacetic acid (CF<sub>3</sub>COOH), ozone (O<sub>3</sub>) and nitrogen dioxide (NO<sub>2</sub>). The functional groups are classified in relation to their reactivity with the probe gases, both in terms of the amount of surface functional groups present as a percentage monolayer of the nanoparticle surface as well as in terms of their uptake coefficient or probability. Several representative examples of commercial, sampled and laboratory–generated nanoparticle substrates will be given.

#### Keywords

Heterogeneous kinetics, gas uptake, probe gases, surface functional groups, surface/interface characterization

#### Introduction

The reactivity of a nanoparticle (NP) including the interaction with biological membranes or substrates leading to deleterious health effects significantly depends on the molecular surface composition as it is the "gateway" to understanding and controlling chemical reactivity of NP's. There are many ways to characterize the surface of NP's, and the following strategy is just a complementary technique to many others existing in the field. Characterization of NP's in use today involve the investigation of the thermal behavior such as pyrolysis and thermogravimetric measurements. The extraction behavior of NP's in terms of the adsorbed (extractable) organic phase vs. the elemental carbon content, OC/EC (Organic Carbon/Elementary Carbon) measurements, WSOC, WinSOC and other extraction strategies have been used in relation to soot characterization. Elemental analysis (C, H, N, O) and surface spectroscopies (XRD, EELS, XPS, EXAFS and others) have been extensively used in the recent past whereby the notion of "surface" has to be understood in relation to the wavelengthdependent penetration depth of the probing radiation. In addition, imaging techniques (ESEM, HRTEM) have successfully been applied to the investigation of NP's. The present contribution proposes to apply a chemical way to characterize the surface of NP's by making use of the chemical reactivity of surface functional groups of NP's gauged by suitable probe gases which "see" only one monolayer.

#### • <u>michel.rossi@psi.ch</u> to whom all correspondence should be addressed **Experimental Apparatus**

A Knudsen flow reactor was used for the investigation of the heterogeneous reaction of the probe gases with the NP substrate presented either on a loaded Teflon membrane filter or as loosely packed powder housed in a FEP Teflon-coated sample cup. The use of a Knudsen flow reactor is suitable because it favors gas-wall collisions compared to gas-gas collisions owing to the low total pressure in the range  $10^{-5}$  to  $10^{-2}$  mbar leading to large mean free paths. Figure 1 displays a two-chamber Knudsen flow reactor that has been used in the present investigations.



Figure 1. Schematic outline of a Knudsen reactor

When the plunger is pulled up the sample compartment housing the sample is exposed to the probing gas. Changes in the molecular beam intensity monitored by phase-sensitive molecular beam modulated electron impact mass spectrometry (MBMMS) is recorded. The number of probe molecules "lost" to the sample is expressed as a fractional number of formal monolayers of the probe gas on the NP surface under conditions of known BET surface of the NP sample. The following reactions are thought to occur on the surface of nanoparticles upon interaction with the six used probe gases (Setyan et al., 2010, and references therein):

-COOH + N(CH<sub>3</sub>)<sub>3</sub> 
$$\rightarrow$$
 -COO<sup>-</sup>(CH<sub>3</sub>)<sub>3</sub>NH<sup>+</sup> (Salt) (1)

 $\begin{array}{l} R_1R_2\text{-}C=O + NH_2OH \twoheadrightarrow R_1R_2\text{-}C(OH)(NHOH) \twoheadrightarrow H_2O \\ + R_1R_2\text{-}C=N\text{-}OH (Oxime) \end{array}$ (2)

B: + HCl/CF<sub>3</sub>COOH  $\rightarrow$  B:H<sup>+</sup>Cl<sup>-</sup>/CF<sub>3</sub>COO<sup>-</sup> (Salt) (3)

$$-C_{red} + O_3/NO_2 \rightarrow -C_{ox} + O_2/N(II \text{ or III})$$
(4)

Equation (1) forms a salt following gas-surface heterogeneous neutralization of trimethylamine. In case of an organic aerosol or soot substrate the acidic site is identified with a carboxylic surface group that represents totally oxidized carbon. In Eq. (2)hydroxylamine probes partially oxidized surface sites such as aldehydes or ketones leading to the corresponding oximes for organic substrates. Hydroxylamine is also a weak base as well as a strong reducing agent which is important for inorganic substrates such as TiO<sub>2</sub>. Equation (3) describes the probing of basic surface sites, either Brönsted or Lewis bases B:. HCl is a weaker acid in the gas phase than trifluoroacetic acid (TFA) which is the reason that the former probes strong, the latter weak as well as strong bases. Equation (4) describes the redox reaction of a strong  $(O_3)$  and a weak  $(NO_2)$  oxidizer interacting with a weakly reducing and a strongly reducing surface site, -Cred, respectively.



Figure 2: Interrogation of the surface functional groups of a soot model nanoparticle by suitable (reactive) probe gases (schematic).

Figure 2 represents different surface NP functional groups interacting with the corresponding probe gases. As an example, TFA is a strong acid in the gas phase and probes basic oxides whereas HCl is too weak an acid to be able to probe these (displayed at the "8 o'clock" position in Figure 2). The difference in response to both HCl and TFA is taken to be a measure of the surface abundance of these basic oxides that do not contain aliphatic (amine-like) or aromatic (pyridine or pyrrole-like) nitrogen. Basic oxides are polycyclic aromatic hydrocarbons that contain an ether linkage and a carbonyl group separated by conjugated double bonds as displayed in Figure 2. Known examples of basic oxides are  $\alpha$  - and  $\gamma$  - pyrones as well as coumarins. The role of basic oxides and other relevant issues involving soot NP's have been introduced by Boehm and coworkers (Boehm, 1994; Boehm, 2002). There are three strong constraints on the properties of chemical reactions in order to qualify as probe reactions: (i) reaction must be fast on the time scale of the gas-residence time in the Knudsen flow reactor so as to enable fast saturation. This corresponds to (pseudo)-first order rate constants on the order of 0.1 s; (ii) the reaction must occur at low total pressures on the order of  $10^{-3}$  mbar or lower; and (3) reaction must be fast on the time scale of the gas residence time at ambient temperature. We have used additional probe gases such as CO<sub>2</sub>, H<sub>2</sub>S, CH<sub>2</sub>O, SO<sub>2</sub>, SOCl<sub>2</sub> and others in order to probe other properties of surface functional

groups. However, the six probe gases presented here have been systematically used for all the samples to be discussed next.

#### **Experimental Results and Discussion**

In the past we have investigated an array of substrates using the proposed surface titration technique which have been summarized in a recent minireview (Setyan et al., 2010). We now report on and discuss four recent results encompassing a variety of substrates of wide-ranging interest.

(A) Diesel soot from incomplete combustion of Diesel and Biodiesel (Hydrotreated Vegetable Oil, HVO) collected from an exhaust manifold of a modern common rail Diesel engine (Tapia et al., 2015). Figure 3 displays two typical uptake curves recorded as MBMMS signal at m/e 46 and 48 corresponding to the uptake of NO<sub>2</sub> and O<sub>3</sub>, respectively, on Diesel soot. A typical experimental run consists of monitoring the MBMMS signal with the sample compartment (SC) closed at a given constant flow rate of NO<sub>2</sub> or O<sub>3</sub> into the flow reactor. Once the MBMMS signal level is established (I<sub>0</sub>) the plunger is lifted in order to expose the solid NP sample to the probe gas until complete or partial saturation of the MBMMS signal. This means that the MS signal does not change with reaction time anymore, either because no uptake is occurring when the original value I<sub>0</sub> has been attained (complete saturation), or when an intermediate steady-state level has been attained owing to continuous uptake at a signal level intermediate between zero and  $I_0$ , namely  $I_{ss}$  (partial saturation, Figure 3). The missing MS signal in terms of an absolute number of molecules that fail to exit the flow reactor and are thus avoiding detection are precisely these molecules that remain adsorbed on the sample and are lost to detection. Once the MS signal levels are constant the plunger is lowered in order to seal the SC again, and the MS signal level rises to the original level  $I_0$  which completes a measurement cycle. By the same token, the initial uptake coefficient  $\gamma_0$  of the probe gas kinetics may be retrieved using these same data by comparing the ratio of  $I_0$  and  $I_{ss}$  in



Figure 3: Titration of Diesel engine soot using NO<sub>2</sub> (upper) and ozone (lower panel)

relation to kesc, the rate constant of escape out of the Knudsen flow reactor for the corresponding probe gas. HVO and Diesel soot samples reacted with all probe gases indicating the presence of different functionalities on the same aerosol surface. In comparison with the reactivity of amorphous carbon PRINTEX XE2-B the investigated soot samples had a significantly higher surface density of reducing functional groups reacting with the O<sub>3</sub> probe gas by a factor of 10 to 30. Noteworthy is the fact that these reducing groups were practically all strongly-reducing because the O<sub>3</sub> and NO<sub>2</sub> probe gas experiments resulted in identical surface densities. These strongly-reducing reactions may elicit distinct catalytic redox reactions in biological systems and may lead to unexpected health effects which is in the process of being explored in more detail.

(B) Commercially available (Sigma-Aldrich) Ag nanoparticles in the presence of  $O_3$  as an oxidizer. The goal of this project was to characterize the elemental surface composition of a noble metal, namely Ag in terms of the extent of surface oxidation. If the NP surface is oxidized we expect the following equilibrium to take place under atmospheric relative humidity:

 $Ag_2O + H_2O \leftrightarrows AgOH$ 

In case the extent of surface oxidation is significant we expect a large amount of surface OH groups that are expected to react with HCl as a probe gas according to eqs. (6a) and (6b):

$$\{AgOH\} + HCl \rightarrow \{AgCl\} + H_2O$$
(6a)  
$$\{Ag_2O\} + 2HCl \rightarrow 2\{AgCl\} + H_2O$$
(6b)

Figure 4 (upper panel) displays the results of the titration of the original Ag NP's using HCl as a probe gas monitored at m/e 36. This curve is a nice example of a reaction that goes to completion (saturation) after a



Figure 4: Uptake of HCl of virgin Ag nanoparticle sample (upper) and O<sub>3</sub>-oxidized sample (lower).

certain time and reveals that the "dip" in the curve represents a loss of a single monolayer of HCl. This means that Ag NP's are covered by a monolayer of Ag<sub>2</sub>O and/or AgOH as we do not currently have the means to distinguish between both forms of oxidized surface. The surface OH groups are strongly acidic as they react to the extent of a single monolayer with TMA as well. Subsequently, the Ag NP was oxidized both by O3 and NO2 to Ag2O/AgOH whereby the relative oxidation rate was 1000:1 commensurate with oxidizing power. Somewhat unexpectedly, the "back titration" by HCl went on to completion to the extent of oxidation chosen previously. Both the oxidizer (NO<sub>2</sub>, O<sub>3</sub>) as well as the probe gas (HCl) diffused without great difficulty across the already oxidized layers of the Ag NP at ambient temperature. Using  $O_3$ approximately 10 molecular monolayers of Ag are oxidized within 45 minutes without reaching saturation, and oxidation went on as a function of time, albeit slowing down with time.

(C) Pure and Cu-doped Hombikat<sup>TM</sup> methanation photocatalyst, focusing on  $CO_2$  and methanol adsorption. Owing to the presence of strongly-acidic OH surface groups on the anatase phase we expected

CO<sub>2</sub> to be a suitable surface probe leading to a surface (bi)carbonate according to the following equation:

Figure 5 (upper panel) in fact shows significant uptake of  $CO_2$  all the way to complete saturation. However, upon pumping  $CO_2$  is desorbing again in a reversible process. The lower panel on Figure 5 shows reversible  $CH_3OH$  adsorption following eq. (8) which is the first requirement for catalytic methanol conversion:

$$Ti-O^{-}H^{+} + CH_{3}OH \rightarrow TiOH \bullet CH_{3}OH$$
(8)

At saturation approximately 75% of a monolayer adsorbs on Cu-doped Hombikat  $TiO_2$  in a reversible fashion. Owing to its larger BET surface compared to standard Evonik P25  $TiO_2$  the present Hombikat catalyst adsorbs six times more CH<sub>3</sub>OH. These results show that quantitative analysis is possible in relation to characterization of industrial catalysts.



Figure 5: Uptake of CO<sub>2</sub> (upper) and CH<sub>3</sub>OH (lower) on TiO<sub>2</sub> powder sample (Hombikat (Sachtleben, D))

(D) Characterization of volcanic ash from various eruptions including synthetic proxies of volcanic glass. Four different volcanic ashes sampled from the corresponding eruptions (Eyjafjallajökull/Iceland, April 2010; Tungurahua/South America, Pinatubo 1991/Philippines, Chaitén/South America) and four synthetic volcanic glasses were chosen for a systematic investigation of its SO<sub>2</sub>, O<sub>3</sub> and HCl uptake behaviour. The volcanic material was expected to have been exposed to gases at an average of 400 to 500°C in the hot plume after eruption, that are often accompanied by major SO<sub>2</sub> and HCl emissions. The adsorption of SO<sub>2</sub> was expected to be mediated by acidic surface OH

groups to lead to a reversibly adsorbed bisulfite analogous to eq. (7). Owing to the instability of bisulfite or sulfite we exposed original and samples previously exposed to  $SO_2$  to the strong oxidizer  $O_3$  in order to investigate potential sulfite to sulphate or S(IV) to S(VI) conversion.



Figure 6: Uptake of SO<sub>2</sub> as a function of SiO<sub>2</sub> content

Figure 6 displays the uptake of  $SO_2$  as a function of the  $SiO_2$  weight content (%wt) of both the volcanic ash (round symbols) and volcanic glass (square symbols) samples. It is evident that the synthetic volcanic glasses take up  $SO_2$  roughly up to ten times as much as volcanic ash. The absolute numbers for  $SO_2$  uptake are in the realm of a few % of a formal monolayer or a fraction thereof. This is a recently opened up new area for this characterization technique that has still to overcome a few technical hurdles, not the least of which is the apparent inhomogeneity of the solid samples. In order to make progress it seems clear that the titration results have to be seconded by complementary auxiliary measurements.

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functional groups at the gas/particle interface of soot from a Diesel engine using Diesel fuel, *Environm. Sci. Poll. Res.* 22(7), 4863.

## Direct observation of ketohydroperoxide formation and decomposition in photolytically initiated oxidation of *n*-butane, neopentane, and diethylketone

#### A. J. Eskola, A. M. Scheer, I. O. Antonov, L. Sheps, J. D. Savee, D. L. Osborn, C. A. Taatjes

Combustion Research Facility, Sandia National Laboratories, 7011 East Avenue, MS 9055, Livermore, California 94551, USA

Understanding kinetics and mechanisms of chain-branching is essential for reliable modelling of autoignition chemistry, which is important for new low-emission, high efficiency engine technologies. In the first steps of fuel oxidation, a fuel radical adds to O<sub>2</sub> forming RO<sub>2</sub> that can isomerize *via* internal H-atom abstraction to form a QOOH radical. This carbon-centered QOOH can again react with a 'second' O<sub>2</sub> forming OOQOOH radical that, after internal abstraction and subsequent dissociation, forms the OH radical and a ketohydroperoxide (KHP). Further decomposition of the labile KHP is believed to produce an oxy-radical (QO) and OH, effectively leading to the release of two OH radicals (chain-carriers) per fuel radical, resulting in chain-branching.

In the current work, product formation in low-temperature (500 K – 700 K) photolytic Cl-atom initiated oxidation of *n*-butane, neopentane, and diethyl ketone was investigated using multiplexed photoionization time-of-flight mass spectrometry (MPIMS) employing the Advanced Light Source synchrotron radiation for ionization. Experiments were performed using a new high-pressure flow-reactor in the pressure range 740 – 2500 Torr, with a few measurements carried out at 4 - 10 Torr using a low pressure reactor. These experiments probe the time-resolved and isomer-specific formation of products following the laser-photolytic initiation of oxidation.

Of the three fuel molecules studied, the mechanism of KHP formation is probably most simple in low-temperature neopentane oxidation because all hydrogens are equivalent and only one QOOH isomer can be formed. In the Cl-atom initiated oxidation of *n*-butane both 1-butyl and 2-butyl radicals are formed, and after reaction with  $O_2$  and isomerization, each of these radicals has three QOOH isomers available, totaling six possible QOOH radicals. The situation is similar for Cl-atom initiated diethylketone (3-pentanone) oxidation, which also can form two initial radicals and six different QOOH radicals. The current work employs partially deuterated *n*-butanes and diethylketones, enabling separation of KHP isomers by mass and identification of the specific QOOH pathways involved. Significant effort was also made to determine KHP decomposition products and reactions channels. Kinetic simulations of experimental results suggest that also other KHP decomposition channels than KHP  $\rightarrow$  QO + OH play important role.

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# A COMPARATIVE STUDY OF BENZENE OXIDATION IN LEAN-TO-RICH LAMINAR PREMIXED FLAMES

Zisis Malliotakis<sup>1</sup>, George Skevis<sup>2,•</sup>, George Vourliotakis<sup>1</sup>, Maria Founti<sup>1</sup>

<sup>1</sup>Laboratory of Heterogeneous Mixtures and Combustion Systems, Thermal Engineering Section, School of Mechanical Engineering, National Technical University of Athens, Heroon Polytechniou 9, Polytechnioupoli-Zografou, Athens

15780, Greece.

<sup>2</sup>Aerosol & Particle Technology Laboratory, Chemical Process & Energy Resources Institute, Centre for Research & Technology Hellas, 6th km Charilaou-Thermi Road, P.O. Box 60361, 57001, Thessaloniki, Greece.

#### Abstract

Laminar premixed benzene flames are important tools for understanding the combustion chemistry of practical fuels with a significant aromatic content. Despite numerous experimental and numerical investigations, uncertainties still exist regarding even major benzene combustion features. A handful of very recent premixed benzene flame data sets offer a unique possibility for the judicious evaluation both of experimental and simulated data under similar or even virtually identical operating conditions. In the present work a total of twelve low pressure, lean-to-rich ( $\varphi$ =0.75-2.0), laminar premixed benzene flames have been numerically investigated. Computations were carried out using a comprehensive detailed kinetic model developed by the authors. The mechanism is shown to successfully reproduce benzene flame structure for the majority of cases. A numerical formalism is developed and utilized to define, through data analysis and mechanism evaluation, appropriate metrics that are able to quantify the range of validity of the mechanism also taking into account experimental uncertainties. The effects of dilution on flame structure and the effect of PAH chemistry not only on emissions but also on the major flame features are also discussed.

#### Keywords

Laminar premixed flames, Detailed kinetic modelling, Benzene chemistry, Uncertainty analysis

#### Introduction

Concerns about environmental pollution have raised an interest in optimizing the combustion of hydrocarbon-based fuels. Incomplete combustion leads both to reduced efficiency and emissions of pollutants, such as oxygenated and aromatic species. Many of these species are currently unregulated but the implementation of future regulations will also rely on an accurate description of their combustion chemistry. The chemistry of benzene, the first aromatic ring, is thus crucial for two reasons. Most hydrocarbon fuels contain a significant aromatic content and benzene is the indicative species for molecular growth and eventual soot formation. The combustion chemistry of benzene in flames has been extensively studied over the last four decades. However, several uncertainties still exist particularly in the early part of benzene oxidation as summarized in e.g. Saggese et al. (2013) and Vourliotakis et al. (2011). A wealth of premixed benzene flame data sets that has recently appeared offers a unique possibility for the judicious evaluation of experimental and modelling uncertainties data under similar or even virtually identical operating conditions. The purpose of this work is to assess the performance of a comprehensive state-of-the-art detailed kinetic mechanism against recently published data and quantify experimental and numerical uncertainties.

#### Detailed kinetic mechanism development

In the present work, a single, comprehensive detailed chemical kinetic mechanism (Vourliotakis et al. 2015) is utilized in order to model and analyze twelve low-pressure laminar premixed benzene flames, see Table 1. The mechanism has been extensively validated against experimental speciation data from counterflow and premixed flames, laminar flame speeds, shock tubes, ignition time delays, perfectly stirred and plug flow reactors, all under a wide range of temperatures, pressures and stoichiometries and for a wide range of fuels. The current version of the mechanism consists of 185 species and 1043 reversible elementary reactions. All computations have been performed using the PREMIX feature of the CHEMKIN software.

The major carbon pathways in Flames E and H are shown in Fig. 1. Although most of the qualitative features are similar there are significant quantitative differences particularly at the early stages of the flame development. In both flames benzene oxidation leads to the phenyl and phenoxy/phenol paths at a branching ratio of 70:30. As the flames get richer the phenoxy path becomes progressively more dominant. The fate of the phenoxy radical is also interesting. In Flame E it forms phenol and decomposes to the cyclopentadienyl radical at almost equal rates. In Flame H the phenol path is unimportant and all phenoxy is channeled to the  $C_5$  chain.

<sup>•</sup> gskevis@cperi.certh.gr

Flame	Φ	C/O	P(Torr)	Xfuel	X <sub>02</sub>	XAr	V(cm/s)	m(mg/cm2s)	Reference
А	0.70	0.31	33.75	3.000	29.00	68.00		2.931	Detilleux and Vandooren (2009)
В	0.75	0.30	30.00	5.910	59.09	35.00	36.10		Yang et al. (2015)
С	1.00	0.45	33.75	3.000	20.00	77.00		2.984	Detilleux and Vandooren (2009)
D	1.00	0.40	30.00	7.640	57.36	35.00	36.10		Yang et al. (2015)
E	1.25	0.50	30.00	9.270	55.73	35.00	36.10		Yang et al. (2015)
F	1.50	0.60	30.00	10.84	54.16	35.00	36.10		Yang et al. (2015)
G	1.75	0.70	30.00	12.32	52.68	35.00	36.10		Yang et al. (2015)
Н	1.78	0.70	30.00	9.500	40.50	50.00		2.100	Yang et al. (2007)
Ι	1.80	0.72	20.03	13.50	56.50	30.00	50.00		Bittner and Howard (1981)
J	2.00	0.82	33.75	12.00	44.00	44.00		3.102	Detilleux and Vandooren (2009)
Κ	2.00	0.80	37.50	11.80	44.20	44.00	35.00		Defoeux et al. (2005)
L	2.00	0.80	30.00	13.68	51.32	35.00	36.10		Yang et al. (2015)

Table 1. Investigated flames



Figure 1. Major reaction carbon paths for Flames E (numbers in black) and H (numbers in parentheses).

Flame stoichiometry also affects the  $C_5H_5/C_5H_6$ equilibration In Flame E most of the former is recycled to the latter through hydrogen abstraction reactions but in the more radical-deficient richer Flame H the loop is broken and cyclopentadiene feeds promptly to the  $C_3$ and  $C_4$  chains.



Figure 2. Comparison of experimental (points) and simulated (lines) CO species data.

Changes in carbon pathways are reflected in major and key intermediate profiles shown in Figs. 2-4 for selected flames. The performance of the mechanism is generally very acceptable and the evolution of species profiles with stoichiometry is accurately captured. An issue of concern is the over-prediction of acetylene and, to a lesser extent, methyl radical levels in the post-flame zone of very rich flames. This is a constant feature of most comprehensive kinetic models and requires further work.



Figure 3. Comparison of experimental (points) and simulated (lines) C<sub>2</sub>H<sub>2</sub> species data.



Figure 4. Comparison of experimental (points) and simulated (lines) CH<sub>3</sub> species data.

The mechanism also successfully captures the evolution of naphthalene levels as function of stoichiometry, as shown in Fig. 5. This indicates that the balancing between oxidation and molecular growth paths is accurately represented. Note that naphthalene is mainly formed through the recombination of cyclopentadienyl radicals.



Figure 5. Comparison of experimental (points) and simulated (lines) naphthalene species data.

#### Phenyl, phenol and phenoxy

The most serious drawback of the mechanism relates to the severe over-prediction of phenol levels. This is in turn related to uncertainties in the rate and product distribution of the  $C_6H_5+O_2$  reaction. Vourliotakis et al. (2011) have shown that there are four possible products for this reaction, namely  $C_6H_5O+O$ ,  $o-C_6H_4O_2+H$ ,  $C_5H_5+CO_2$  and  $C_5H_5O+CO$ .



Figure 6. Comparison of experimental (points) and simulated (lines)  $C_6H_5OH$  and  $C_5H_6$  species data in Flames D (a) and L (b). Grey lines correspond to the revised mechanism.

Channeling the reaction exclusively to  $C_6$  products leads to severe phenol over-predictions. On the other hand, use of a branching ratio (7:1) in favour of the  $C_5$ path leads to excellent phenol and cyclopentadiene levels, see Fig. 6. However, discrepancies still exist in lean flames. Clearly further theoretical work is required although there is recent evidence in favour of the  $C_5$ path (e.g. Tanaka et al., 2012).

# Experimental uncertainties and dilution effects

The wealth of flame datasets examined in this study make it possible to quantify experimental uncertainties and assess their influence on modelling. Figures 7-8 compare temperature and species data from the virtually identical Flames J and K – only differing slightly in the temperature profiles. This however is insufficient to explain the (more than a factor of 2) differences in key intermediate species profiles (such as  $C_3H_4$ ). This can be a measure of measurement uncertainty, but complicates modelling efforts.



Figure 7. Measured temperature profiles (stars) and comparison of experimental (dots) and simulated (lines) C<sub>6</sub>H<sub>6</sub> species data



Figure 8. Comparison of experimental (points) and simulated (lines)  $C_3H_4$  species data.

The effects of varying dilution levels can be analysed by examining Flames C and D which vary in the levels of Ar dilution. This results in significant temperature differences and the rates of fuel (and oxygen) decay. Major species are also affected (at a ratio close to the dilution ratio) since their levels are mainly controlled by pressure dependent reactions with rates largely determined by diluent levels. On the other hand stable intermediates are not seriously affected.



Figure 9. Measured temperature profiles (stars) and comparison of experimental (dots) and simulated (lines)  $C_6H_6$  species data.



Figure 10. Comparison of experimental (points) and simulated CO<sub>2</sub> species data (lines)



Figure 11. Comparison of experimental (points) and simulated (lines) C<sub>2</sub>H<sub>2</sub> species data.

# Conclusions

In the present work a total of twelve premixed benzene flames have been numerically investigated using a comprehensive detailed kinetic model developed by the authors. The mechanism is shown to successfully reproduce benzene flame structure for most cases. It has been shown that the early branching of phenyl radical consumption to the  $C_6$  and  $C_5$  chains is crucial in controlling key flame features. The effect of dilution on flame structure is also quantified.

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Figure 12. Comparison of experimental (points) and simulated (lines) H<sub>2</sub> species data

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# REACTION CH<sub>3</sub> + CH<sub>3</sub> → C<sub>2</sub>H<sub>6</sub> STUDIED OVER THE 292 – 714 K TEMPERATURE AND 1 – 100 BAR PRESSURE RANGES

Manuvesh Sangwan<sup>a</sup>, Chao Yan<sup>a</sup>, Evgeni N. Chesnokov<sup>b</sup> and Lev N. Krasnoperov<sup>a\*</sup> <sup>a)</sup>New Jersey Institute of Technology, Newark, NJ 07102, USA <sup>b)</sup>Institute of Chemical Kinetics and Combustion, Novosibirsk 630090, Russia

# Abstract

Reaction of recombination of methyl radicals,  $CH_3 + CH_3 \rightarrow C_2H_6$  (1) was studied using pulsed laser photolysis coupled to transient UV-vis absorption spectroscopy over the 292 - 714 K temperature and 1 - 100 bar pressure ranges (bath gas He), very close to the high pressure limit. Methyl radicals were produced by photolysis of acetone at 193.3 nm or in the reaction of electronically excited oxygen atoms O(<sup>1</sup>D), produced in the photolysis of N<sub>2</sub>O at 193.3 nm, with CH<sub>4</sub>, and subsequent reaction of OH with CH<sub>4</sub>. Temporal profiles of CH<sub>3</sub> were recorded via absorption at 216.36 nm and 216.56 nm. The absolute intensity of the photolysis light inside the reactor was determined by an accurate *in situ* actinometry based on the ozone formation in photolysis of N<sub>2</sub>O/O<sub>2</sub>/N<sub>2</sub> mixtures. The rate constant of reaction 1 in the high-pressure limit has a negative temperature dependence:  $k_{1,inf} = (5.66 \pm 0.43) \times 10^{-11} (T/298 \text{ K})^{-0.37} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1} (292 - 714 \text{ K}).$ 

#### Keywords

Methyl radicals, recombination, rate constant, high pressure limit.

#### Introduction

Recombination of methyl radicals is important in hydrocarbon pyrolysis and combustion:

$$CH_3 + CH_3 \rightarrow C_2H_6$$
 (1)

Reaction 1 is a chain termination step, the rate of this reaction affects the self-ignition thresholds, flame propagation speed, as well as other parameters of hydrocarbon combustion. In methane combustion, this reaction is responsible for production of C2 hydrocarbons. Reaction 1 is important for fundamental chemical kinetics and is considered as a benchmark reaction for testing and improving theories of radical - radical reactions as a simplest reaction of recombination of hydrocarbon free radicals. Precise knowledge of the kinetic parameters of reaction 1 is nessassary in laboratory studies of other reactions involving methyl radical. In relative kinetic studies involving methyl radicals, reaction 1 was frequently used as a reference reaction.

Due to the importance of reaction 1 to the field, it was extensively studied both experimentally and theoretically. There are numerous publications associated with the kinetics of reaction 1 (Manion et al. 2008, Blitz et al. 2015). Although reaction 1 has been studied across a wide temperature range, only a few studies were conducted at pressures high enough for more reliable determination of the rate constant in the high pressure limit. Hippler et al. (Hippler et al. 1984) studied reaction 1 over the pressure range 1 - 210 bar at ambient temperature in two bath gases, argon and

nitrogen, using laser photolysis coupled to transient UV absorption. The high pressure limit was reached at ca. 10 bar of Ar (within the experimental uncertainty), the determined recombination rate constant in the high pressure limit is  $k_{1,\infty} = 5.8 \times 10^{-11}$  cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup>. A drop of the measured recombination rate constant at higher pressures (ca. 12% in Ar and ca. 3 times in N<sub>2</sub> at 210 bar) was attributed to the onset of diffusion control.

The main motivation of the current work was extension of the study to cover a temperature range from ambient to elevated temperatures (293 - 714 K) in the conditions of only minor deviations from the high pressure limit.

### Experimental

The approach is based on the excimer laser photolysis coupled to UV-Vis transient absorption spectroscopy and to a high-pressure flow system. Helium was used as a bath gas in all experiments. The measurements were performed over the 1 - 100 bar pressure and 19 - 441 °C (292 - 714 K) temperature ranges. The total flow rates of the reactant mixtures with helium were in the range 340-4600 sccm. The temperature profiles are uniform within  $\pm 5$  K in the reactants zone. Average temperature in the reactant zone is taken as the reactor temperature.

Acetone - water mixtures (mole fraction of acetone in water was varied from 0.02 to 0.04) were injected into the evaporator of the high pressure flow system using a precision syringe pump. The flow rate of acetone-water mixtures was varied in the range of 0.5 – 10  $\mu$ L/min depending upon the reactor pressure

<sup>\*</sup>To whom all correspondence should be addressed

and temperature. The concentrations of the precursors used:  $(0.1 - 1.0)x10^{17}$  molecule cm<sup>-3</sup> for N<sub>2</sub>O, (0.87 - $(6.76) \times 10^{15}$  for CH<sub>3</sub>COCH<sub>3</sub> and  $(1.4 - 7.0) \times 10^{17}$  for H<sub>2</sub>O. The laser photon fluence inside the reactor was varied in the range  $(2.4 - 15) \times 10^{15}$  photons cm<sup>-2</sup> pulse<sup>-1</sup>. The initial concentrations of methyl radicals were in the range  $(5 - 46) \times 10^{13}$  molecule cm<sup>-3</sup>. The measurements were performed over the 1 - 100 bar (He) pressure and 292 – 714 K temperature ranges. The concentrations of the radicals precursors were monitored downstream the reactor by an on-line quadrupole mass-spectrometer. No noticeable depletion of the radical precursors (acetone and nitrous oxide) was observed at and below above 714 K. The repetition rate of the laser was set to ensure complete replacement of the gas mixture in the reactor between the pulses (0.1 - 1 Hz depending upon the reactor pressure).

In situ actinometry. The absolute concentrations of CH<sub>3</sub> radicals were determined based on the photon fluence inside the reactor, the absorption cross-sections of N<sub>2</sub>O and acetone at 193.3 nm, and the efficiency of conversion of O(1D) atoms produced in the photolysis of N<sub>2</sub>O/CH<sub>4</sub> mixtures to CH<sub>3</sub> radicals. The latter was typically ca. 0.79x2 and was accurately evaluated using a reaction mechanism The photon fluence inside the reactor was measured using an in situ laser light actinometry, based on the ozone formation, a stable molecule with very well characterized crosssection at the monitoring wavelength. Formation of ozone in the photolysis of N2O/O2/N2 mixtures at 1 bar and 298 K was monitored at 253.6 nm.

 $CH_3$  radicals generation and monitoring. CH<sub>3</sub> radicals were generated either by excimer laser pulse photolysis of acetone or of N<sub>2</sub>O in the presence of methane at 193.3 nm (ArF excimer laser). The major processes are:

$(CH_3)_2CO + hv(193 nm)$	$\rightarrow$	$2CH_3 + CO$	(2)
$N_2O + hv(193 nm)$	$\rightarrow$	$O(^{1}D) + N_{2}$	(3)
$O(^{1}D) + CH_{4}$	$\rightarrow$	$OH + CH_3$	(4)
$OH + CH_4$	$\rightarrow$	$H_2O \ + CH_3$	(5)

The decay of methyl radicals was monitored by absorption at 216.36 nm and 216.56 nm (1200 groove/mm grating, 300 mm focal distance, both slits 0.25 mm, triangle slit function, FWHM = 0.64 nm) using 75 W (Oriel) short arc xenon lamp combined with an imaging spectrometer (Acton 300i).

A 75 W xenon short arc lamp was used as a light source. In some experiments the lamp intensity was increased (ca. 100 times at 216 nm) by current boosting to 50 A using Photon Technology International MCP2010 pulser. The imaging spectrograph (Acton 300i) is equipped with three diffraction gratings (1200, and two 150 groove/mm), a PMT (Hamamatsu R106) with a preamplifier (EMI) and a gated intensified CCD (ICCD) camera (ICCD Max, Roper Scientific). The residual light from the excimer laser pulse is blocked using a liquid filter

 $(4.3 \times 10^{-2} \text{ M solution NaCl in water, 1 cm})$ . The liquid filter provides virtually complete absorption of 193 nm light. A photomultiplier tube (Hamamatsu R106) mounted on the exit slit operates on a reduced number of dynodes (6) with a large high voltage divider current (maximum 2.7 mA), which ensures good linearity and lower noise at high photon fluxes. The typical anode current is 10 to 20 µA. The PMT signal is preamplified (EMI preamplifier), digitized and stored using a digital storage oscilloscope (LeCroy 9310A, Dual channel, 400 MHz, 100 Msamples/s, 50 Kpts/ch). The time resolution is determined by the preamplifier setting and can be 0.03, 0.3, 3, or 30 usec. Typically, a 0.3 µsec time constant was used (the measured actual rise time  $t_{0.1-0.9}$  is 0.46 µsec). The traces are accumulated (500 to 5000 pulses) and transferred to a PC for processing. The ICCD camera installed on the second outlet of the spectrograph is used to record absorption spectra of transient as well as stable species.

# Results

Absorption spectrum of CH<sub>3</sub> radicals is temperature and pressure dependent. Detailed analysis of the absorption spectrum for the  $\tilde{B}^2A_1' \leftarrow \tilde{X}^2A_2$ " in the vicinity of 216 nm as well as a review of previous experimental measurements and modeling is given in a recent paper of Blitz et al.(Blitz et al. 2015) The individual rotational lines are strongly broadened by predissociation, therefore, the spectrum has no rotational structure.

To understand the changes in the apparent cross-section of methyl radical taken with a finite spectral slit widths, we recorded the absorption band at 216 nm with the highest resolution achievable in the current experimental set-up (1200 groove/mm, focal distance 300 mm, slit width 10 um, camera pixel size of 30 um) using current boosted Xe arc lamp and a gated ICCD camera. A 75 W Xe short arc lamp was boosted up to 50 A for 7 ms. The spectra were taken 0.9 usec after the laser pulse (delayed by ca. 6 ms after the beginning of the boosting pulse) with the time gate of 2 usec. Increasing pressure to 100 bar leads to a substantial broadening of the spectrum accompanied with a blue shift of the maximum (Hippler et al. 1984) of ca. 0.22 nm at 100 bar.

In the kinetic measurements, wider slits (0.25 mm) were employed. This corresponds to the triangular spectral slit function with the FWHM = 0.64 nm. Convolution of the spectra obtained with 10 um slit and ICCD detection with the triangular FWHM =0.64 nm slit function shows almost no impact on the widths of the spectra with some reduction of the maximum apparent cross-section. It is most pronounced at 1 bar and ambient temperature, where the maximum cross-section of the convoluted spectrum drops by  $12 \pm 3\%$ . The wavelength of the maximum of the apparent cross-section shifts with temperature and pressure. In the current study, two central wavelengths were used: 216.36 nm, which corresponds to the small hole in the

main peak and the maximum apparent cross-section at ambient temperature and pressure when taken with the resolution of 0.64 nm, and 216.56 nm, which correspond to the maximum of the high resolution spectrum.

In the calculations of the reactants concentrations small deviations from the ideal gas behavior were taken into account. The compression factor for He is 1.0471 at 300 K and 1 bar. The deviations decrease at low pressures and higher temperatures.

Apparent absorption cross-sections of methyl radicals were measured with the triangular spectral slit function with FWHM = 0.64 nm using the two central wavelengths, 216.56 nm and 216.36 nm.

The measurements have been performed in the sub-millisecond time domain. Recombination of methyl radicals (1) is the only major elementary reaction responsible for the decay of methyl radicals. Modeling with the detailed mechanism using numerical solution of the corresponding system of differential equation showed that the impact of the inclusion of water photolysis on the resulting rate constant 1 does not exceed 1.5%.

Maximum scatter of the experimental data (observed at high temperatures and pressures) does not exceed  $\pm 16\%$ . Both photolysis systems produce consistent results indistinguishable within the experimental scatter.

Investigation of the kinetic results reveals two major features. First, there is a systematic drop in the measured apparent rate constant at 100 bar pressure as compared with the measurements at 1 bar. Second, no rise of the apparent rate constant was observed within the accuracy of the measurements at 714 K, where some rise due to the pressure fall-off potentially could be expected.

Drop of the rate constant with pressure could be caused by several factors. It could be due to the quenching of the primary photolysis processes 2 and 3. Due to the large difference in the complexity of the two precursors, acetone and N<sub>2</sub>O, this cause does not seem to be probable. Another possibility would be the onset of the diffusion control. And, finally, closely associated with the diffusion control, cage effects in the photolysis of the precursors as well as reaction 4 might be responsible for the drop of the initial concentrations of methyl radicals in the bulk, and, hence, the apparent rate constant.

In application to reaction 1a the impact of diffusion controlled was discussed by Hippler et al. (Hippler et al. 1984) The observed in this work 15 to 20 % drop at ambient temperature corresponds to the diffusion controlled rate constant of  $k_{diff} = (2.3-3.3) \times 10^{-10}$  cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup>. For an isotropic reaction of spherical particles A and B the diffusion controlled rate constant is  $k_{diff} = 4\pi R_{AB} D_{AB} = 4\pi (R_A + R_B)(D_A + D_B)$ . For a self-reaction A+A, like the recombination of methyl radicals, this expression should be divided by 2, resulting in  $k_{diff} = 8\pi R_A D_A$ . Estimating D(CH<sub>3</sub>-He) as

 $D(CH_4-He) = 0.73 \times 10^{-2} \text{ cm}^2 \text{s}^{-1}$  at 293 K and 100 bar leads to the radius R=0.015 nm = 0.15 A. However, recombination of methyl radicals is highly anisotropic, and a more realistic estimate of the "reactive spot" size is ca. 0.38 nm = 3.8 A. This estimates show that potentially diffusion control might play some role at 100 bar.

Decrease of the rate constant of methyl radicals recombination was observed previously by Hippler et al.(Hippler et al. 1984) at ambient temperature in argon and nitrogen bath gases. The observed drop of the rate constant in Ar was ca. 4% at 100 bar and ca. 12% at 210 bar, smaller than that observed in He in this work (ca. 15-20% at 100 bar). Much larger drop was observed when nitrogen was used as the bath gas, ca. factor of two at 100 bar and ca. factor of three at 200 bar.(Hippler et al. 1984) Neither the scale of the effects nor the relative order for different bath gases correspond to the diffusion control limited by translational diffusion of the reactants. In view of highly anisotropic interaction of methyl radicals orientation relaxation rather than translational diffusion might be responsible for the observed decrease in the recombination rate.

The second feature is the absence within the experimental accuracy of any rise of the rate constant with pressure at 714 K over the range 1 - 100 bar. Estimates based on the recommended low pressure limit rate constant  $k_0(714 \text{ K}) = 5.28 \times 10^{-28} \text{ cm}^6 \text{molecule}^ ^{2}$ s<sup>-1</sup> and the high pressure rate constant of  $3.14 \times 10^{-11}$ cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup> (Baulch et al. 1994) lead at 1 bar and 714 K to the ratio  $x=k_0[M]/k_{inf} = 171$ . Both the extrapolations based on the standard Troe formalism (Troe 1979) and the recent approach of Zhang and Law (Zhang and Law 2009) result in the prediction of ca. 25% drop of the rate constant at 1 bar compared with the 100 bar value. Accepting more recent low pressure limit rate constant of Wang et al. (Wang et al. 2003)  $k_0(714 \text{ K}) = 2.21 \times 10^{-27} \text{ cm}^6 \text{molecule}^{-2} \text{s}^{-1}$  leads to much higher  $x=k_0[M]/k_{inf} = 714$ . Using this ratio and the Zhang and Law expressions leads to a smaller deviation of the rate constant at 1 bar from the high pressure limit of ca. 11%. However, the most recent of the revisions broadening factor in dissociation/recombination reactions by Troe and Ushakov show that the previous expressions overestimated the breadth of the transition region at high  $x = k_0[M]/k_{inf}$  values (i.e., very close to the high pressure limit).(Troe and Ushakov 2011, Troe and Ushakov 2014) The predicted deviation of the rate constant from the high pressure limit at 714 K and 1 bar does not exceed 5%. It should be much smaller at higher pressures taken into account in the averaging (1, 3, 10 and 30 bar). Therefore, we estimate the error associated with the fall-off effects at 714 K as not exceeding 2 %. Based on these estimates, no pressure dependence of the rate constant within the experimental error is expected in accord with the experimental observations.

In view of no pressure dependence observed within the experimental error over the 1 - 30 bar pressure range and a small drop of the rate constant at 100 bar we took average of all measurements over the range 1 -30 bar as the high pressure rate constant of reaction 1. The results are shown in Fig. 1. The results were fitted by the expression:

Several experimental and theoretical studies are also shown in Fig. 1 for comparison. There is excellent agreement at room temperature, and slight difference in the temperature dependence. Current experimental results are in excellent agreement with the theoretical



Figure 1. Dotted circles - rate constant  $k_1$  in the high pressure limit over the temperature range 292 - 714 K (this work). Solid line – fit with expression 6. Dash-dotted line – Wang et al. 2003, dashed line -Klippenstein et al. 2006 (theory), dotted line - Robertson et al. 1995.

study of Klippenstein et al.(Klippenstein et al. 2006) over the whole temperature range of this study. At elevated temperatures of this study, the rate constant determined in this work is slightly higher than that obtained by the data extrapolation to the high pressure limit in the most recent experimental study of Wang et al.(Wang et al. 2003) (ca. 17% at 714 K).

#### Conclusions

Reaction of recombination of methyl radicals was studied over an elevated pressure (1 - 100 bar) and temperature ranges (292 - 714 K). Currently, at elevated temperatures, these measurements are the closest to the high pressure limit. Slight drop of the rate constant at 100 bar is reported. The rate constant in the high pressure limit exhibit negative temperature dependence, in accord with the previous studies. The low temperature data are in good agreement with the

literature, the results at the elevated temperatures are slightly higher than in the previous measurements, and in excellent agreement with the theoretical calculations of Klippenstein et al. (Klippenstein et al. 2006)

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# HIGH-TEMPERATURE AUTOIGNITION STUDY OF 2-METHYL FURAN AND 2-METHYL TETRAHYDROFURAN

Mazen A. Eldeeb, Shirin Jouzdani, Lingshu Zhang, Ben Akih-Kumgeh\* Department of Mechanical and Aerospace Engineering, Syracuse University, Syracuse NY 13244, USA Email: bakihkum@syr.edu

#### Abstract

High-temperature ignition delay times of methyl furan (2-MF) and methyl tetrahydrofurans (2-MTHF) are measured in a shock tube. The experiments are carried out using homogeneous gaseous mixtures of fuel, oxygen, and argon in stoichiometric proportions where the argon to oxygen ratio is maintained at 3.76. The current experiments are carried out at average pressures of 3 atm over a temperature range of 1060 - 1300 K. In addition to ignition delay time measurements, fuel concentration profiles during ignition are obtained by means of laser absorption spectroscopy using a HeNe laser at a fixed wavelength of  $3.39 \ \mu$ m. With respect to ignition delay times, it is observed that under similar conditions of equivalence ratio, argon/oxygen ratio, pressure, and temperature, 2-MTHF has longer ignition delay times than 2-MF. Ignition delay times are compared with the predictions from recent chemical kinetic models of both fuels and it is observed that both models generally predict shorter ignition delay times than measured. The relatively high absorption cross-section of 2-MTHF at  $3.39 \ \mu$ m allows for concentration profiles to be determined and compared to simulation predictions. In line with the observed discrepancy in ignition predictions, predicted 2-MTHF concentration profiles are such that the fuel is more rapidly consumed. For the stoichiometric mixtures studied, complete conversion of the fuel into radicals and oxidation products coincides with the ignition event. The low absorption cross-section of 2-MF is concentration species, so that their appearance makes it impossible to quantify the temporal 2-MF concentration profiles within reasonable uncertainty bounds.

#### Keywords

Furans, tetrahydrofurans, ignition delay times, speciation, laser absorption spectroscopy.

#### Introduction

Furans are among bio-derived chemicals that are considered for use in combustion systems as alternatives to the current petroleum fuels. In addition to investigating the compatibility of the proposed fuels with current engine components, fundamental combustion studies are needed to guide the development of mathematical models for computational engine design and control. Recent research efforts on the fundamental combustion properties have established key mechanistic pathways during pyrolysis and oxidation. These results have been used in developing chemical kinetic models. Experimental studies have yielded data sets on autoignition and flame propagation. Further work is needed to relate observed differences to chemical structure. It is the objective of this research project to extend the body of knowledge by investigating ignition of various furans and tetrahydrofurans in a comparative manner that sheds light on possible reaction pathway differences.

The most investigated fuel from the furan class is 2,5-dimethylfuran (2,5-DMF). Previous work has explored the mechanistic pathways and detailed chemical kinetic models have been developed (Sirjean et al. (2013); Somers et al. (2013)). Engine studies and

experimental studies have since followed these early studies and this progress has recently been reviewed by Qian et al. (2015). From our previous work (Eldeeb and Akih-Kumgeh, 2014), we have established the ignition behavior of furan, 2-MF, and 2,5-DMF. Apart from 2,5-DMF, experimental investigations and detailed modeling of 2-MF have been carried out (Wei et al., 2013; Tran et al., 2014, Uygun et al., 2014). Similar to 2,5-DMF, there is increasing literature on the oxidation of this system but further work is needed in order to improve the prediction capabilities of existing and new chemical kinetic models. The saturated furans, tetrahydrofurans, are equally attractive as fuel additives or pure fuels. Although not as extensively studied as 2,5-DMF and 2-MF, there are increasingly more research activities on their computational and experimental characterizations (Simmie, 2012; Moshammer et al., 2013; Uygun et al., 2014; Sudholt et al., 2015). Although the number of ignition investigations of furans is increasing, few studies focus on structure-activity trends. This endeavor can yield further insight on major controlling pathways. Further. measurements of species concentration profiles during furan oxidation or pyrolysis in shock tubes have not been reported before. These profiles are needed to further constrain models beyond validations based on prediction of global kinetics such as ignition delay times.

We investigate the ignition behavior of mixtures of 2-MTHF, oxygen, and argon at temperatures above 1000 K in a shock tube reactor at pressures of about 3 atm. The results are put in the broader context of furan reactivity by comparing with the ignition data of 2-MF. In addition to ignition delay time measurements, concentration profiles of fuel are obtained using mid infra-red laser absorption techniques in a shock tube. Fuel concentrations profiles are measured using a He-Ne laser emitting at 3.39  $\mu$ m. The datasets will further serve as validation targets for current and future chemical kinetic models of furan.

#### **Experimental approach**

Experiments are carried out in a shock tube reactor with an internal diameter of 10 cm, a test section length of 6 m and a total length of 9 m. Behind the reflected shock waves, the test mixture is subjected to high temperature and pressure conditions, enabling the approximation of the experiment as a constant volume adiabatic reactor for modeling purposes. Leading up to ignition, the temperature is fairly constant since endothermic elementary reactions compete with exothermic reactions until the system approaches ignition upon conversion of the fuel to radicals and partial combustion products. Shock arrivals are determined from pressure signals measured using fast-response pressure transducers. The post shock temperature is calculated from equations of motion of a 1D shock wave, accounting for variable specific heats. The shock velocity needed for calculations is determined from shock arrival times at pressure transducers that are mounted at known separations from one another. Data acquisition is by means of a high frequency National Instrument Digitizer.

Test mixtures of fuel, oxygen and argon are prepared in a 150-liter mixing tank using the manometric techniques. Partial pressures are measured using an MKS Baratron pressure transducer with a range of 1000 torr. The fuels, 2-MF and 2-MTHF, are both of 99+ % purity; oxygen and argon are research grade gases from Airgas. Post-reflected shock conditions are determined using the CalTech detonation tool kit in CANTERA with thermodynamic data taken from chemical kinetic models by Somers et al. (2013) and Moshammer et al. (2013).

Uncertainty in the calculated temperature is the main source of error in the reported ignition delay time data and is estimated to be 20-30 K in this study, which could translate to an ignition delay uncertainty of about 30 % at 1000 K. The uncertainties are related to precise determination of shock velocity and initial compositions and conditions. The ignition delay times in this study are within 2 ms, so that the effect of preignition pressure rise can be considered not to strongly undermine the assumption of a constant volume reactor. Ignition delay times are determined based on CH chemi luminescence signals as illustrated in Figure 1 for a stoichiometric mixture of 2-MTHF.

Simulations of ignition delay times and fuel concentration profiles are carried out using the CANTERA software package.

Laser absorption measurements in this preliminary work are focused on fuel concentration measurements using a fixed wavelength He-Ne laser at 3.39  $\mu$ m. This will be extended to carbon monoxide measurement at 4.58  $\mu$ m. We use the direct absorption technique at a fixed wavelength. The number density of an absorbing medium, *N*, along a path, *L*, is related to the attenuation of the laser intensity of characteristic wavelength through the Beer-Lambert's Law:

$$\frac{I}{I_o} = \exp(-\sigma(p,T)NL)$$

 $I_0$  and I are the laser intensities in front of and behind the absorbing medium, respectively. The absorption cross-section,  $\sigma$ , is a function of temperature and pressure that needs to be determined. In this work, this is determined in the shock tube before experiments and after the incident and reflected shock waves, making use of the known composition of the manometrically prepared test mixtures. The cross-sections, as observed in previous work on a number of hydrocarbons (Klingbeil et al. (2006)), decrease as the shock pressures and temperature increase.



Figure 1. Representative ignition profile for a mixture of 2-MTHF/O2/Ar at a pressure of 3.3 atm.

#### Preliminary results and discussions

Ignition delay times of stoichiometric mixtures in argon bath, with an argon to oxygen ratio, *D*, of 3.76 at nominal pressures of 3 atm are shown in Figure 2. It is observed that the ignition delay times of the saturated furan, 2-MTHF are longer than those of the unsaturated 2-MF up to a factor of 2 under certain temperature conditions. The experimental observations are

compared with model predictions using a combined furan model by Somers et al. (2013) and the 2-MTHF model by Moshammer et al. (2013). As can be seen, both models under predict the ignition delay times. Measured delay times are higher by about a factor of 2. The observed reactivity trend is qualitatively shown at the higher temperature end. Regarding the trend, it is considered that addition reactions to C=C bonds in 2-MF and its early radicals are likely to yield more reactive radicals and favorable pathways than in the case of the saturated 2-MTHF. Further model analysis and considerations of possible improvements are currently undertaken. Further determining the rate at which carbon monoxide is formed during pyrolysis and ignition could further shed light on the pathway differences associated with fuel molecular structures.



Figure 2. Ignition delay times of 2-MF and 2-MTHF at a nominal pressure of 3 atm. Model predictions: 2-MTHF, red – model by Moshammer et al. (2013) and 2-MF, blue: model by Somers et al. (2013).

Temporally resolved profiles of species concentrations serve as more rigorous validation targets for chemical kinetic models. Figure 3 shows the species concentration profiles of 2-MTHF at three different conditions. The average absorption cross section of the mixture behind reflected shock waves is 12 m<sup>2</sup>/mol and from model analysis, the concentration other hydrocarbon intermediates are of the order of ppm, so that from previous knowledge cross section of small species (Klingbeil et al., 2006; Mevel et al., 2012) and these low concentrations, the absorbance is attributed to fuel concentration except in the vicinity of the ignition event. As seen in Figure 2, both models considered in this study under predict the ignition delay times. From the curvature of the simulation profile at 1105 K and the experiment at 1179 K, it can be seen that improving the model to adequately predict the ignition delay time would bring the model prediction into closer agreement with the experimentally determined fuel concentration profiles.



Figure 3. Concentration profiles of 2-MF at three conditions. The profiles are compared with predictions using the model by Somers et al. (2013).

In the case of 2-MF, the absorption cross section behind reflected shock waves (of the order of 1 m<sup>2</sup>/mol) are quite small relative to those of methane (20 m<sup>2</sup>/mol) and other low carbon species typically observed in oxidation and pyrolysis products. Once these intermediates are formed in reasonable amount they contribute to the observed absorbance, so that it cannot be fully attributed to the original fuel. In Figure 4, it would imply that the fuel concentration increases after reaction onset before disappearing at the instance of ignition. Nevertheless, the absorbance approaches zero for stoichiometric mixtures just before ignition onset as the fuel, together with intermediates capable of C-H bond stretch activity, are consumed. The absorption cross sections of furan at 3.39  $\mu$ m are too low to be detected by the current absorption set up. This is similar to the aromatics compound, where benzene is hardly detectable at 3.39  $\mu$ m but the cross section increases with the degree of alkylation.



Figure 4. Concentration profiles of 2-MF at three conditions. The profiles are compared with predictions using the model by Somers et al. (2013).

**Future work** 

Ongoing research on 2-MF and 2-MTHF characterization is focused on applying the laser absorption technique with a fixed wavelength DFB Quantum Cascade laser at 4.58  $\mu$ m to quantify CO production during ignition and pyrolysis. Ongoing computational chemistry calculations are focused on bond dissociation calculations.

#### Conclusion

Ignition delay times of 2-MF and 2-MTHF have been measured behind reflected shock waves at pressures of 3 atm and over a temperature range of 1060 K to 1300 K. Quantitative fuel concentration profiles of 2-MTHF have been determined using fixed wavelength laser direct absorption at 3.39  $\mu$ m. These profiles have been compared to model predictions. It is observed that 2-MTHF has longer ignition delay times than 2-MF, with differences of about a factor of 2. The reactivity difference is tentatively attributed to possible radical attack on the unsaturated carbon double bonds in 2-MF, that result in more reactive radicals and possibly, diradicals. Current models under predict the ignition delay times and consequently lead to much faster fuel depletion rates than observed in experiments for 2-MTHF. The absorption cross-section of 2-MF under these conditions are too low that intermediate species with C-H bond stretch activity are likely to influence the observed laser absorbance. This work establishes the relative ignition behavior of 2-MF and 2-MTHF applicable to fuel design. The data set presented in this work will be useful in further validating models

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# INFLUENCE OF OXYGENATION IN CYCLIC HYDROCARBONS ON CHAIN-TERMINATION REACTIONS FROM R + O<sub>2</sub>: TETRAHYDROPYRAN AND CYCLOHEXANE

Brandon Rotavera<sup>\*</sup>, John D. Savee, Ivan O. Antonov, Haifeng Huang, Leonid Sheps, Judit Zádor, David L. Osborn, and Craig A. Taatjes<sup>\*</sup> Combustion Research Facility, Sandia National Laboratories Livermore, CA 94551

Keywords

Lignocellulosic biofuel, Pyran, Autoignition, Chemical kinetics.

The use of biofuels in internal combustion engines that are derived from lignocellulosic biomass serves to augment the use of conventional, petroleum-based transportation fuels. Due to the molecular composition of lignin and cellulose, lignocellulosic biofuels contain varying degrees of oxygenation. Tetrahydropyran (c-C<sub>5</sub>H<sub>10</sub>O) is a cyclic ether and a component in lignocellulosic biofuels. It is analogous to cyclohexane (c-C<sub>6</sub>H<sub>12</sub>) by replacement of a methylene group (CH<sub>2</sub>) with an oxygen atom (Fig. 1), and is also base-model cyclic ether intermediate formed in low-temperature oxidation reactions of linear alkanes starting from *n*-pentane. Integrating tetrahydropyran as a blending component with conventional transportation fuels requires fundamental insight into its autoignition characteristics, particularly reactions that affect low-temperature chain-branching initiated by R + O<sub>2</sub>. The propensity of a conventional or bio-derived hydrocarbon to undergo low-temperature chain-branching depends partly on the competition from propagation reactions, leading to cyclic ether intermediates, and partly on termination reactions, where instead of the R + O<sub>2</sub> reaction sequence leading to QOOH + O<sub>2</sub> and subsequent chain-branching, the initial oxidation steps proceed through reactions leading to low-reactivity hydroperoxy radicals (HOO).

To examine the influence of oxygen on chain-termination pathways stemming from  $R + O_2$  reactions, Cl-initiated oxidation of tetrahydropyran and cyclohexane were conducted using two different experiments: multi-plexed photoionization mass spectrometry (MPIMS) and two-tone frequency modulation multi-pass near-infrared (NIR) laserabsorption spectroscopy. MPIMS experiments were conducted at 8 Torr and 500 – 750 K to measure photoionization spectra and branching fractions for chain-termination channels, utilizing synchrotron radiation at the Chemical Dynamics Beamline of the Advanced Light Source, and quantitative HOO time profiles were measured in the multi-pass NIR experiments using a diode laser tuned to 6625.784 cm<sup>-1</sup> at 20 Torr from 500 – 750 K.



Fig. 1. Molecular structures of tetrahydropyran and cyclohexane.

# A LOW PRESSURE FLAME STUDY OF 2-BUTYLTETRAHYDROFURAN

Alena Sudholt<sup>1,\*</sup> Pierre-Alexandre Glaude<sup>2</sup>, Frédérique Battin-Leclerc<sup>2</sup>, and Heinz Pitsch<sup>1</sup>

<sup>1</sup>Institute for Combustion Technology, RWTH Aachen University, 52056 Aachen, Germany <sup>2</sup>Laboratoire Réactions et Génie des Procédés (LRGP), CNRS, Université de Lorraine, ENSIC, 54001 Nancy, France

#### Abstract

An experimental study of the oxidation behavior of 2-butyltetrahydrofuran in a stoichiometric premixed low-pressure flat flame has been performed. Axially resolved speciation data is measured by means of gas chromatography with flame ionization and thermal conductivity detectors. Detection limits of a few ppm are reached for all investigated hydrocarbons, oxygenates, and carbon oxide species. Species profiles for the major combustion products and intermediates such as carbon monoxide, carbon dioxide, water, hydrogen, and a variety of hydrocarbon species are presented. Further, oxygen profiles have been obtained. High levels of  $C_2$  and  $C_3$  intermediates, a large variety of  $C_4$  hydrocarbons and oxygenates as well as minor levels of larger hydrocarbons in the  $C_5$  to  $C_7$  range were measured. Generally, the dominance of alkene intermediates was evident throughout the whole study.

# Keywords

Low pressure flat flame, Species measurements, 2-Butyltetrahydrofuran

#### Introduction

Ever increasing anthropogenic carbon dioxide emissions are the driving force behind the search for efficient, sustainable transportation fuels from lignocellulosic biomass. This search has led to a broad variety of potential biofuel candidates. Enzymatic and catalytic conversion processes can be applied to transform cellulose into platform molecules such as levulinic acid, itaconic acid, and hydroxymethylfurfural and finally into furanic and hydrofuranic species. While the economic and energetic viability of the production pathways are important measures for the selection of potential biofuels, not all possible fuel candidates promise equally well performance in internal combustion engines. In recent years, 2-methylfuran (2-MF) (Tran et al., 2014), 2,5-dimethylfuran (2,5-DMF) (Román-Leshkov et al., 2007, Somers et al., 2013), and 2-methyltetrahydrofuran (2-MTHF) (Moshammer et al., 2013) were discussed extensively as novel biofuels and many detailed kinetic studies have been performed. However, 2-MF, 2,5-DMF, and 2-MTHF are gasoline replacements and the investigation of potential diesel fuel replacements from lignocellulosic biomass is less advanced. In an initial study of the global ignition characteristics of bio-derived furans and hydrogenated furans with

• a.sudholt@itv.rwth-aachen.de

larger side chains, 2-butyltetrahydrofuran (2-BTHF) was found to be a promising diesel candidate (Sudholt et al., 2015) with a derived cetane number of 45.5 and therewith fulfills the ignitability criterion for diesel fuels in the US market and is close to the requirements in the EU. The molecular structure of 2-BTHF is shown in Figure 1.



Figure 1: 2-Butyltetrahydrofuran

The combustion behavior of 2-BTHF is largely unknown and an investigation of 2-BTHF in a laminar premixed flat flame at low pressure is therefore performed to obtain insight into its detailed oxidation behavior at high temperatures.

#### Low pressure flame experiments

The experimental setup consists of a vertically displaceable McKenna burner located in a vacuum chamber and a quartz glass micro probe with which gas samples are drawn from the flame.



Figure 2: Flat flame burner with micro probe in a vacuum chamber.

The samples are taken on-line and evaluated with gas chromatographs. A brief overview of the experimental setup and procedure is given in the following and a schematic of the setup is shown in Figure 2. Further experimental details are given in Tran (2013) and Tran et al. (2014). The oxidizer applied for these measurements is an oxygen/argon mixture. Similar to Tran et al. (2014), the pressure in the vacuum chamber is set to 50 Torr (6.66 kPa) and the argon dilution to 77 mol%. The total volume flow through the burner is 5.4  $l_N/min$ . The burner temperature however is set to 363 K instead of the previously used 333 K to minimize condensation at the burner surface. For the controlling of the liquid fuel flow, a Bronkhorst Cori-Tech mini coriolis mass flow controller with an accuracy of  $\pm 0.2\%$  of the reading value plus  $\pm 0.2$  g/h is applied; all gaseous flows (oxygen, argon, and methane) are set using Bronkhorst thermal mass flow controllers with an accuracy of  $\pm 0.5\%$  of the reading value. The liquid fuel is vaporized with argon in a Bronkhorst CEM-system (controlled evaporation and mixing) and subsequently mixed with oxygen and methane before being introduced into the McKenna burner. All lines between the vaporizer and the burner are heated to prevent 2-BTHF condensation.

#### Species measurements

An axially resolved species analysis is performed and 36 major intermediate and product species are identified and quantified using gas chromatographs. All hydrocarbon and oxygenated species, water and most permanent gases are analyzed using an Agilent 7890A gas chromatograph equipped with a HP-Plot Q column and a HP-Molsieve, a thermal conductivity detector (TCD) and a flame ionization detector (FID) with methanizer. The applied carrier gas is helium. Note that a separation of argon and oxygen cannot be achieved with this setup. Hence, a second gas chromatograph is used and hydrogen and oxygen are quantified with an HP 5890 gas chromatograph equipped with a carbo-sphere column and a TCD.



Figure 3: Fuel consumption.

The utilization of argon as carrier gas allows for the quantification of oxygen without the need for a separation of argon and oxygen in the column. The gas chromatographic measurements are calibrated using appropriate calibration gas mixtures. The detection limit of the FID is in the range of a few ppm for all relevant hydrocarbons, oxygenates, and carbon oxide species, whereas the detection limit for water, hydrogen, and oxygen is 50 ppm on the TCD. This results in an error of  $\pm 5\%$  for the major species and  $\pm 10\%$  for the minor species with mole fractions of less than 100 ppm (cf. Tran et al., 2014). The oxygen/argon oxidizer allows for leak detection and quantification of the vacuum system via nitrogen measurements, as any detected nitrogen enters the system solely through air leakage in the sample line. All species measurement results are corrected for that air leakage in the data post processing. Note that only for oxygen, the molar amount of the species itself changes. For all other species merely the relative mole fractions are adjusted.

#### **Results and discussion**

In Figure 3, it is shown that 2-BTHF is fully consumed in the flame at approximately 3 mm height over the burner (HOB). In Figure 4, the intermediate and product species profiles are presented. Initially, only a small increase of carbon dioxide is detected. A higher gradient occurs until the fuel is consumed at 3 mm HOB. Then, a lower rise of the CO<sub>2</sub> concentration is measured. An exponential increase of the H<sub>2</sub>O concentration is obtained until 3 mm HOB. Afterwards, the H<sub>2</sub>O levels stay approximately constant. A major intermediate in the 2-BTHF flame is ethylene with a maximum concentration of 2.12 mol%. The ethylene concentration is approximately linear until a HOB of 2 mm. At 3 mm HOB, ethylene is mostly consumed. The maximum acetylene concentration is 4900 ppm. Of the same order are the concentrations of ethane (4300 ppm), formaldehyde (5900 ppm), and propene (5700 ppm). The species profiles of acetylene and ethane have a similar shape than that of ethylene, whereas for many other species, especially the oxygenates and larger unsaturated hydrocarbons, the concentrations close to their maximum



Figure 4: Intermediate and product species profiles in the 2-BTHF flame.



Figure 5: 2-BTHF decomposition reactions.

values are already reached at 1 mm HOB and remain relatively unchanged until they are consumed at 3 mm HOB. Other intermediate species detected in significant quantities are propane (1100 ppm), 1butene (1700 ppm), 1,3-butadiene (1200 ppm), acetaldehyde (880 ppm), and 1-hexene (1100 ppm), and propanal (470 ppm). Also found in minor concentrations are several C<sub>4</sub> species: 2-butanone (320 ppm), butanal (111 ppm), 2-butenone (108 ppm), 2butene (75 ppm), 2-butenal (31 ppm), and 1,2butadiene (8 ppm). Further, a variety of unsaturated C5 and higher hydrocarbons were measured: 1pentene (100 ppm), 2-pentene (107 ppm), isopentenes (61 ppm), trans-1,3-pentadiene (128 ppm), cis-1,3-pentadienes (81 ppm), 2-hexene (41 ppm), and 1-heptene (251 ppm).

In Figure 5, selected decomposition pathways are shown. The C-H bond dissociation energies of 2-BTHF (Sudholt et al., 2015) show weaker C-H bonds adjacent to the oxygen atom. The ring opening hence most probably occurs at the locations depicted in Figure 5 and lead to linear oxygenated C<sub>8</sub> radicals which subsequently decompose via  $\beta$ -scission. The resulting stable species ethylene and 1-hexene were found to be major intermediates of the 2-BTHF flame. However, such long linear radicals as produced from the ring opening of 2-BTHF can follow many different decomposition and oxidation pathways. The presented speciation data will hence proof to be valuable when determining branching ratios of the oxidation reaction pathway.

# Conclusion

A fundamental experimental study of the oxidation of 2-BTHF was performed and species profiles for oxygen, hydrogen, carbon monoxide, carbon dioxide, water, and hydrocarbon species, including oxygenated species and separated isomers, were presented. Typical intermediate species occurring in flames, e.g. hydrocarbons and oxygenates with carbon numbers of one and two, were measured. With mole fractions around 5000 ppm, formaldehyde, acetylene, ethane, and propane were identified as major intermediates in 2-BTHF oxidation. Further, ethylene and 1-hexene as a direct products of the consumption reactions of fuel radicals, such as ring opening and the first  $\beta$ -scission, were detected. Larger unsaturated hydrocarbon

species were obtained in significant amounts, especially 1-butene, and 1,3-butadiene. Aldehydes and ketones with carbon numbers of three and four were also found to be important intermediates.

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# The Multichannel Reaction of O(<sup>3</sup>P) with Cyclopentene

John D. Savee<sup>\*</sup>, Judit Zàdor, Xiaohu Li, Ahren Jasper, Craig A. Taatjes and David L. Osborn Combustion Research Facility, Sandia National Laboratories Livermore, CA 94551-0969

### Abstract

The reaction of  $O({}^{3}P)$  with cyclopentene has been investigated at 4 Torr and 298 K using multiplexed synchrotron photoionization mass spectrometry. Under these conditions we find that the main reaction product formed after addition of  $O({}^{3}P)$  to cyclopentene is the  $C_{5}H_{8}O$  isomer propylketene. We also observe minor contributions from the acrolein + ethene and 1-butene + CO bimolecular channels, the latter of which has not been previously observed experimentally. Our determination of propylketene as the almost sole  $C_{5}H_{8}O$  isomer is in significant disagreement with previous gas chromatography studies carried out at 200 Torr that identified cyclopentene oxide, cyclopentanone, cyclobutylcarboxaldehyde as the major  $C_{5}H_{8}O$  products. Recent calculations have identified pathways leading to these products, but to date no pathway forming propylketene has been identified. To this end, the present work also demonstrates the use of the newly developed program KinBot to perform rigorous searches for available pathways on the lowest-lying singlet and triplet  $C_{5}H_{8}O$  potential energy surfaces relevant to the title reaction.

#### Keywords

O(<sup>3</sup>P), cyclopentene, intersystem crossing, combustion, KinBot

# Introduction

O(<sup>3</sup>P) is a critical oxidizer in combustion environments and it is thus important to understand not only the rate coefficients for its reaction with hydrocarbons but also the products of these reactions. For the case of O(<sup>3</sup>P) reacting with small linear unsaturated hydrocarbons, addition reactions tend to dominate H-abstraction at low temperatures and pressures. Pioneering crossed molecular beams experiments have shown that in many cases these additions reactions are heavily mediated by intersystem crossing (ISC) from the initial triplet adduct to lowerlying singlet electronic states (Casavecchia et al., 2005). The non-adiabatic interactions that govern intersystem crossing in these systems are difficult to account for computationally, and thus experimental signatures of the dynamical processes at play in these reactions of upmost importance in efforts to create predictive combustion models.

Currently, experiments yielding isomerresolved accounts of the products of these reactions have proven to be useful in this regard. Using spin conservation arguments and aided by quantum chemical calculations, unimolecular and bimolecular products observed experimentally can often be traced back to mechanistic pathways that occur on triplet or singlet potential energy surfaces (i.e., whether ISC occurred prior to product formation). To date, versatile isomer-resolved methods have been used to study all linear unsaturated  $C_2$  and  $C_3$  species.

However, reactions of O(<sup>3</sup>P) with cyclic unsaturated hydrocarbons have not been studied by

these versatile isomer-resolved techniques. In the present work we report an investigation into the reaction of  $O(^{3}P)$  with the prototypical cyclic alkene cyclopentene.

$$O(^{3}P) + c - C_{5}H_{8}$$
 (R1)

Previous gas chromatography experiments probing R1 at several temperatures and near 200 Torr identified major products of the reaction to be stable isomers of the  $C_5H_8O$  adduct (R1a-R1c) and an active bimolecular channel producing acrolein + ethylene (R1d) (Cvetanovic et al., 1971).

$$O(^{3}P) + c - C_{5}H_{8} \rightarrow$$



$$C_3H_4O + C_2H_4 \tag{R1d}$$

Recent quantum chemical calculations have indeed identified plausible pathways leading to these products (Zhao et al., 2014), all of which must occur after ISC based on spin conservation.

We have recently shown that multiplexed photoionization mass spectrometry can be used as an isomer-resolved probe of  $O(^{3}P)$  + unsaturated hydrocarbon reactions (Savee et al., 2012, Savee et al., 2015). The present work continues our studies of  $O(^{3}P)$  reactions via a reinvestigation of R1. As will be discussed in Ghent, we see very little evidence for the C<sub>5</sub>H<sub>8</sub>O producing channels R1a-R1c, and instead we see evidence that propylketene (R1e) is the primary product of R1.



In accordance with the past experimental study, we observe the bimolecular channel R1d. However, we also see direct evidence for another bimolecular channel, R1f.

$$CH_2 = CHCH_2CH_3 + CO$$
 (R1f)

Because pathways to R1f were not identified in the recent computational study of R1, we have decided to explore this system using KinBot, a new software being developed that automates the exploration of potential energy surfaces. In Ghent we will also present the results of this re-exploration of the  $C_5H_8O$  potential energy surface and its implications for the title reaction.

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# COMPUTATIONAL STUDY OF THE CYCLOPENTYL + O<sub>2</sub> AND METHYCYCLOPENTYL + O<sub>2</sub> REACTIONS

Mariam El Rachidi1\*, Judit Zádor<sup>2</sup> and S. Mani Sarathy<sup>1</sup>

<sup>1</sup>Clean Combustion Research Center, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia <sup>2</sup>Combustion Research Facility, Sandia National Laboratories, MS 9055, Livermore, CA 94551, USA

#### Abstract

Cycloalkanes are significant constituents of conventional fossil fuels, but little is known concerning their combustion chemistry and kinetics, particularly at low temperatures. This study investigates the pressure dependent kinetics of several reactions occurring during low-temperature cyclopentane combustion using theoretical chemical kinetics. The reaction pathways of the cyclopentyl +  $O_2$  adduct is traced to alkylhydroperoxide, cyclic ether,  $\beta$ -scission and HO<sub>2</sub> elimination products. The calculations are carried out at the UCCSD(T)-F12b/cc-pVTZ-F12//M06-2X/6-311++G(d,p) level of theory. The barrierless entrance channel is treated using variable-reaction-coordinate transition state theory (VRC-TST) at the CASPT2(7e,6o) level of theory, including basis set, geometry relaxation and ZPE corrections. 1-D time-dependent multiwell master equation analysis is used to determine pressure- and temperature-dependent rate parameters of all investigated reactions. Tunneling corrections are included using Eckart barriers. Comparison with cyclohexane is used to elucidate the effect of ring size on the low temperature reactivity of naphthenes. The rate coefficients reported herein are suitable for use in cyclopentane and methylcyclopentane combustion models, even below ~900 K, where ignition is particularly sensitive to these pressure-dependent values.

#### Keywords

Cyclopentane, methylcyclopentane, computational oxidation kinetics, pressure-dependent rate constants

# Introduction

Cycloalkanes are significant constituents of transportation fuels, particularly of those derived from oil sands and shale (Westbrook, 2005). They also have a greater propensity for soot formation via dehydrogenation than their non-cyclic counterparts (McEnally and Pfefferle, 2004). Therefore, adequate knowledge of cycloalkane chemistry and kinetics is needed in order to improve fuel combustion efficiencies and reduce emission profiles. Generally speaking, cycloalkane chemistry is similar to that of *n*-alkanes; however, the ring structure and the ring strain have an effect on the rate coefficients of some reactions. For example, cyclohexane is significantly less reactive than *n*-hexane, as evidenced by its longer ignition delay times in rapid compression machines (Tanaka et al., 2003), as well as its higher octane number (API, 1958). This is due to the fact that the ring structure in cycloalkanes suppresses some low temperature chain branching pathways, particularly peroxyalkyl / alkylhydroperoxide isomerizations. When these pathways are suppressed, alternative pathways, namely HO<sub>2</sub> elimination, become more important, resulting in higher

concentrations of olefins compared to non-cyclic hydrocarbons (Yang et al., 2010). The cyclic olefins produced from naphthenes slow ignition and may contribute to soot formation in the high-temperature (i.e. post-ignition) regime.

A more profound understanding of cycloalkane oxidation chemistry requires knowledge concerning the reactivity and degradation kinetics of these compounds. Sirjean et al. (Sirjean et al., 2009) provide theoretical rate parameters of several important low temperature combustion reactions of cyclopentane. including peroxyalkyl alkylhydroperoxy isomerization, and cyclic ether formation, using CBS-QB3 computations. However, they did not consider HO<sub>2</sub> elimination and alternative isomerization pathways; nor did they consider pressure dependence of the kinetic rate constants. The purpose of this study is to determine pressuredependent kinetic rate constants of the low temperature cyclopentane combustion reactions lying on the cyclopentyl +  $O_2$  potential energy surface, using computational methods. The implicated methods allow for the evaluation of the contribution of formally direct pathways, which has been shown to be significant at low pressures (Fernandes et al.,

<sup>\*</sup> Corresponding author: mariam.elrachidi@kaust.edu.sa

2009). The kinetics of methylcyclopentane oxidation is also investigated in order to elucidate the effect of branching on reactivity.

#### **Computational kinetics**

The reaction pathways of the fuel radical + O<sub>2</sub> adduct are traced to alkylhydroperoxide, cyclic ether,  $\beta$ -scission and HO<sub>2</sub> elimination products. The geometries and frequencies of stable chemical species and transition states are calculated at the M06-2X/6-311++G(d,p) level of theory; whereas accurate energies are determined using UCCSD(T)-F12b/cc-pVTZ-F12. Conformational analyses. geometry and frequency calculations are accomplished using the Gaussian 09 suite of programs (Frisch et al., 2009), and the MOLPRO software (Werner et al., 2012) was used for the CCSD(T) calculations. The barrierless O<sub>2</sub> addition step is treated using variable-reaction-coordinate transition state theory (VRC-TST) at the CASPT2(7e,6o) level of theory (Georgievskii and Klippenstein, 2003a; Georgievskii and Klippenstein, 2003b). 1-D hindered rotor treatment was applied to the torsional modes. The pressure-dependent rate parameters of all investigated reactions are determined by solving the time-dependent multiwell master equation for the temperature range 300-2500 K, at pressures 0.001, 0.01, 0.1, 1, 10 and 100 bar. The rate coefficients of the formally direct pathways obtained directly from the solution of the multi-well master equation. Tunneling corrections are included using Eckart barriers. The master equation was

solved using the empirical  $\langle \Delta E_{down} \rangle = 200 \text{ x}$ (T/300)<sup>0.85</sup> cm<sup>-1</sup> exponential-down energy transfer parameterization. Implemented by the PAPER (Predictive Automated Phenomenological Elementary Rates) code (Georgievskii et al., 2013).

#### **Results and discussion**

Figure 1 depicts the potential energy surface of the cyclopentyl + O<sub>2</sub> reaction, calculated at the UCCSD(T)-F12b/cc-pVTZ-F12 level of theory. The energy values are reported relative to that of cyclopentyl + O<sub>2</sub>. As shown in Figure 1, the 3- and 4memebered ring transition states involved in the inter-conversion between the QOOH species have energies that are much higher than the entrance channel (17 and 24 kcal mol<sup>-1</sup>, respectively). The contribution of these channels, including the formally direct pathways that involve skipping through the neighboring wells will be negligible. Thus these two barriers were not included in the ME analysis. The cyclopentyl +  $O_2$  oxidation kinetics on this surface is characterized by 132 irreversible reactions, 24 of which connect adjacent reactants, wells or bimolecular products. The temperature and pressure dependent rate constants of these reactions are fitted to the modified Arrhenius equation using the method of least squares in order to determine the rate parameters A, n and  $E_a$  (pre-exponential factor, temperature coefficient and activation energy, respectively) at each pressure.



Figure 1. Cyclopentyl +  $O_2$  potential energy surface. Energy values in kcal mol<sup>-1</sup> calculated at the UCCSD(T)-F12b/cc-pVTZ-F12 level of theory and reported relative to the cyclopentyl +  $O_2$  energy.

The fitted rate constants of the cyclopentyl + O<sub>2</sub>, peroxyalkyl/alkylhydroperoxy and cyclic ether formation reactions are plotted in Figure 2 at different pressures. The plots depict the expected falloff at lower pressures and higher temperatures. The high pressure limit rate constants of the isomerization and cyclic ether formation reactions are compared to those calculated by Sirjean et al. (Sirjean et al., 2009) at the CBS-QB3 level of theory (Figure 2) The CBS-QB3 rate constants at the high pressure limit are in reasonable agreement with the values calculated herein (less than a factor of 10 difference), except for the cyclic ether formation reaction whose CBS-QB3 rate constants are up to 23 times greater than those calculated using ab initio methods and ME analysis. Meanwhile, the rate coefficients for  $O_2$ addition and HO<sub>2</sub> elimination are compared to the cyclohexane analogs, which are calculated using ab initio methods (Fernandes et al., 2009; Knepp et al., 2007). The comparison shows that the calculated rates of both compounds are relatively similar, with those of cyclohexane being up to 4 times slower in the case of  $O_2$  addition and up to 24 times faster in the case of HO<sub>2</sub> elimination.



Figure 2. Pressure-dependent fitted rate constants for O<sub>2</sub>-addition, isomerization and concerted HO<sub>2</sub> elimination reactions. The fitted high pressure (HP) limit rate constants are compared to the values generated by the ME analysis (HP parameters) as well as to those calculated by Sirjean et al. (Sirjean et al., 2009) at the CBS-QB3 level of theory and those of analogous cyclohexane reactions calculated by Fernandes et al. (Fernandes et al., 2009; Knepp et al., 2007).

#### **Conclusions and perspectives**

The kinetics of the cyclopentyl +  $O_2$  reaction pathways has been investigated theoretically using ab initio methods and master equation analysis over a wide range of temperatures and pressures relevant to combustion modeling. These reaction pathways have a strong influence on low temperature chain branching and thus, accurate rate parameters are required for predictive modeling.

The potential energy surface comprises some low-lying barrier, which shows that the contribution of formally direct pathways to the reactivity of the system is significant, particularly at lower pressures and higher temperatures where collisional stabilization of the chemically activated adduct is minimal.

The calculated rate parameters may be used to simulate the combustion of cyclopentane under a wide range of conditions. The calculated energies may also be used to evaluate the thermodynamic properties of the chemical species involved.

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# A HIGH TEMPERATURE EXPERIMENTAL AND THEORETICAL KINETIC STUDY FOR THE REACTION OF TETRAHYDROFURAN WITH HYDROXYL RADICALS

Binod Raj Giri<sup>\*1</sup>, Fethi Khaled<sup>1</sup>, Milán Szőri<sup>2</sup>, Béla Viskolcz<sup>2</sup> and Aamir Farooq<sup>\*1</sup>

<sup>1</sup> Clean Combustion Research Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Saudi Arabia

<sup>2</sup> Department of Chemical Informatics, Faculty of Education, University of Szeged, Boldogasszony sgt. 6 H-6725 Szeged, Hungary

\*Corresponding author: binod.giri@kaust.edu.sa; aamir.farooq@kaust.edu.sa

#### Abstract

In this study, the reaction of tetrahydrofuran (THF) with OH radicals was investigated behind reflected shock waves over a wide range of experimental conditions (T = 802 - 1338 K,  $p \approx 1.5$  atm) using laser absorption technique to monitor OH radicals near 306.69 nm. Hydroxyl radicals were generated by thermal decomposition of tert-butyl hydroperoxide. The best fit of experimental data on the THF+OH reaction yields the modified Arrhenius expression:  $k_{THF+OH}(T) = 0.09 \cdot \left(\frac{T}{K}\right)^{4.25} \cdot \exp\left(\frac{3525K}{T}\right) cm^3 mol^{-1}s^{-1}$ . High-level quantum chemical calculations were performed to explore important elementary reactions for the THF+OH reaction system. Our calculations at the CCSD(T)/cc-pV(D,T)Z//MP2/aug-cc-pVDZ level of theory reveal that the reaction of THF and OH proceeds either *via* indirect or direct H-abstraction from various sites and directions. It was found that the kinetics of THF + OH can be reasonably described by canonical transition state theory (CTST) which is able to deduce the temperature-dependence of rate coefficients and branching ratio of the formation of tetrahydrofuran-2-yl (THF-R2) and tetrahydrofuran-3-yl (THF-R3) radicals. The calculated rates are compared with the ones obtained from our experiments and the agreement is quite reasonable. To our knowledge, this is the first direct experimental and theoretical kinetic study for the reaction of tetrahydrofuran with OH radicals.

#### Keywords

Tetrahydrofuran, Hydroxyl Radicals, Cyclic Ethers, Quantum Chemical Calculations, Rate Coefficients.

#### Introduction

Cyclic ethers are important combustion species formed during the low-temperature gas phase oxidation of various fuels (Hakka et al. 2009) (Minetti et al. 1995). The mechanism for the formation of cyclic ethers via hydroperoxy alkyl radical (•QOOH) during the oxidation of hydrocarbons is well established (Buda et al. 2005). Among cyclic ethers, five membered cyclic ethers (e.g., tetrahydrofuran) are by far the most abundant oxygenated products (Hakka et al. 2009) (Minetti et al. 1995). Hence, the chemistry involving cyclic ethers plays crucial role in determining the ignition behavior of hydrocarbon fuels. Coupled with the abundance and importance of hydroxyl radicals in combustion systems, the reaction of cyclic ethers with OH carries much importance. In the last two decades, thermal decomposition, kinetics and ignition behaviors of cyclic ethers have been the focus for several researchers. The first study on THF decomposition dates back to 1946 where a heated bulb is used to span the temperature range of 803-943 K (Klute and Walters 1946). It was only in 1986 that Lifshitz (Lifshitz et al. 1986) revived the study of the pyrolysis of THF at high temperature using a shock tube facility. His work spans the temperature range of 1070-1530 K and enabled the elucidation of the main pyrolysis routes of THF at high temperatures. Dagaut et al. conducted a detailed experimental and modeling investigation on the ignition and oxidation of THF at high temperatures (Dagaut et al. 1998). Their kinetic sub-mechanism was chosen in this work to describe the THF chemistry. The aim of this work is to experimentally measure the reaction of THF with hydroxyl radicals (R1) at high temperatures (800-1300 K) and theoretically estimate the branching ratio of the possible products (See *Figure 1*):

$$THF + \cdot OH \rightarrow products \qquad (R1)$$



Figure 1: Possible H-abstraction channels of THF by OH radical

#### **Experimental Setup**

All experiments presented in this work have been conducted in the low pressure shock tube facility (LPST) at King Abdullah University of Science and Technology (KAUST). Only a brief description of this facility is presented herein. Details of the shock tube can be found elsewhere (Badra et al. 2014). The shock tube has 9-meter long driver and driven sections. The driver section length can be reduced to 6 m or 3 m depending on the test time needed to perform the experiments. Only a 3 m driver section length was used in the current work. Optical windows are installed at the sidewall 20 mm from the endwall of the shock tube. Hydroxyl radicals are measured by probing the  $R_1(5)$ absorption line in the (0,0) band of the A<sup>2</sup>  $\Sigma^+ \leftarrow X^2 \Pi$ system near 306.7 nm. Measured OH absorbance signal is converted to concentration using the Beer-Lambert law. Hydroxyl radicals were produced by rapid thermal decomposition of tert-butyl hydroperoxide (TBHP), which is known to be a clean OH precursor and has been validated in many studies (Vasudevan et al. 2005). A 70% TBHP in water solution and Tetrahydrofuran (99.9%) were obtained from Sigma Aldrich. A high-purity, electro-polished, Teflon-coated mixing vessel was used to prepare the mixture of THF and TBHP in argon. The concentrations of reactants were chosen based on sensitivity analysis and pseudo-first-order restrictions.

#### **Computational Details**

To explore the energetic feature of the important reaction channels, molecular structures were optimized at the MP2/aug-cc-pVDZ level of theory (Dunning 1989); (Hehre et al. 1986); (Moller and Plesset 1934); (Woon and Dunning 1993) applying the 'tight' convergence criterion of the Gaussian09 program package. Normal-mode analysis is also carried out for each stationary point of potential energy surface (PES) and the MP2/aug-cc-pVDZ vibrational wavenumbers were scaled by a factor of 0.9615, adopted from Refs (Giri et al. 2010; Merrick and Leadbeater 1979). Similar to previous works (Bansch et al. 2013; Izsak et al. 2009), the non-relativistic limit was approximated in a way that Feller extrapolation (Feller 1992) was applied for HF energies (using ccpVXZ basis sets, where X=D, T and Q) (Dunning 1989; Woon and Dunning 1993) and Helgaker extrapolation for CCSD(T) correlation energies was utilized (Helgaker et al. 1997) with cc-pVDZ and ccpVTZ basis sets (Watts et al. 1993). Therefore, CCSD(T)/cc-pV(D,T)Z//MP2/aug-cc-pVDZ level of theory is chosen to establish a high-level description of the reactive PES. In order to get pre-reactive complexes (RC) as well as post reaction complexes (PC) corresponding to the transition states (TS), characterized, intrinsic reaction coordinate (IRC)

calculations (Gonzalez and Schlegel 1989; 1990) were also carried out at MP2/aug-cc-pVDZ level of theory.

#### **THF + OH Rate Coefficients**

The methyl-butanoate mechanism of NUIG (Dooley et al. 2008) has been selected to model the OH mole fraction time evolution. TBHP sub-mechanism was added to model the TBHP decomposition behind reflected shock waves. Details about the TBHP submechanism and the updated rate constants can be found in Lam's experimental work on methyl-butanoate + OH reactions (Lam et al. 2012). The sub-mechanism of tetrahydrofuran was taken from Dagaut's work on the oxidation of THF at high temperatures (Dagaut et al. 1998). The resulting mechanism was used to perform sensitivity analysis of the OH time profile under our experimental conditions (see Figure 2). The OH concentration profile is primarily sensitive to the Habstraction by OH reaction. Measurements of (R1) were conducted in the temperature range of (847-1285 K) using a mixture of 201 ppm THF with TBHP diluted in argon.



Figure 2: OH sensitivity for a mixture containing 201 ppm THF with 17.5 ppm TBHP and 50 ppm water diluted in Argon. T = 1091 K and P = 1.69 atm.

The rate coefficient of R1 is calculated by fitting the the experimental OH time profile with simulated OH profile. A representative case is shown in *Figure 3*.



Experimentally determined rate coefficients are listed in *Table 1* and plotted in *Figure 4* along with previous estimation (Dagaut et al. 1998) and TS calculations from this work. The best fit of our experimental results (802 K-1338 K) yields the following modified Arrhenius expression  $(cm^{3}mol^{-1}s^{-1})$ :

$k_{THF+OH}(T) = 0.09 \cdot$	$\left(\frac{T}{K}\right)^{4.25}$	• exp	$\left(\frac{3}{2}\right)$	525K T	)	•

Table	1.	Measured	rate	coefficients	of	reaction R1
unic	1.	measurea	ruic	coefficients	$v_{I}$	reaction MI

Temperature	Pressure	<b>k</b> 1
(K)	(atm)	(cm <sup>3</sup> ·mol <sup>-1</sup> ·s <sup>-1</sup> )
802	1.73	1.70E+13
880	1.61	1.77E+13
921	1.5	1.63E+13
960	1.49	1.67E+13
1091	1.69	1.84E+13
1174	1.61	2.12E+13
1240	1.39	2.20E+13
1268	1.73	2.28E+13
1338	1.39	2.55E+13



Figure 4: Arrhenius plot of the rate coefficients of THF + OH reaction: circles (experiments), solid line (fit to experimental data), dashed line (TS calculations), dash-dotted lins (Dagaut et al. 1998)

**Theoretical Study of THF + OH Reaction** 



Figure 5: PES diagram (including zero-point correction) for THF+OH reactios

Our QM calculations have proven that the abstraction reaction can proceed *via* direct and indirect

channels (Figure 5). For the latter, either formation of a van der Waals complex (RC(vdW)) or hydrogenbonded pre-reaction complex (RC(HB)) can be the first elementary step. In the case of weakly bonded RC(vdW) (-4.7 kJmol<sup>-1</sup>), the oxygen of the OH radical is oriented toward the THF hydrogens, while the interaction of the H atom of the OH radical with the O atom of the ether in RC(HB) is significantly stronger (-24.7 kJmol<sup>-1</sup>). Energy levels for transition states of all H-abstractions starting from RC(HB) complex are lower than the reactants. The lowest lying TS corresponds to the H-abstraction from vicinity of the ether group ( $\Delta E_0(TS-2A) = -11.0 \text{ kJmol}^{-1}$ ) resulting in the formation of weak PC-R2A complex of the tetrahydrofuran-2-yl (THF-R2) radical and water. The other TS of R2 with  $\Delta E_0$ (TS-2B) = -9.4 kJmol<sup>-1</sup> leads to the same PC. Because of the exoergicity of reaction R2 (-103.0 kJmol<sup>-1</sup>), this complex rapidly decomposes to give THF-R2 and H<sub>2</sub>O. The complex of RC(HB) is also correlated to the transition state of the Habstraction from the position 3 (R3) which is energetically less favored (TS-3A, -1.7 kJmol<sup>-1</sup>). The relative energy of the post-reaction complex (PC-3A) is similar to the PC-2A, but the stability of free tetrahydrofuran-3-yl (THF-R3) radical is less by 17.9 kJmol<sup>-1</sup> compared to free tetrahydrofuran-2-yl radical (THF-R2). Another indirect H-abstraction channel of R3 is started from the van der Waals complex RC(vdW) and its barrier height is close to zero (TS-3B, 1.7 kJmol<sup>-1</sup>). Even the direct H-abstraction (TS-3C) which leads to THF-R3 and H<sub>2</sub>O has a small barrier height (3.6 kJmol<sup>-1</sup>).

The kinetics of THF + OH can be reasonably well described (Figure 4) by canonical transition state theory (CTST) with molecular and transitions state data from QM calculations, with the assumption of an equilibrium between the reactants and the RCs. The branching ratio of THF-R2 and THF-R3 radicals can also be estimated. In these CTST calculations, all species were assumed to be in the electronic ground state except OH, for which the electronic partition function was calculated with a spin orbit splitting of 139.7 cm<sup>-1</sup> (Herzberg 1989). Tunneling correction is not considered due to the high temperatures of the current work. From Table 2, it is obvious that at lower temperature, the formation of THF-R2 is predominant, but as one would expect, the pathways via the higher lying TS3 transition states gain importance as T increases resulting in excess formation of THF-R3 radical above 1050 K.

Table 2: CTST rate constants and branching ratios

Т	k2,CTST	k3,CTST	k1,CTST	k2/k3
(K)	(	cm <sup>3</sup> ·mol <sup>-1</sup> ·s <sup>-1</sup>	)	
800	8.44E+12	4.51E+12	1.29E+13	1.87
900	8.90E+12	6.00E+12	1.49E+13	1.48
1000	9.61E+12	7.80E+12	1.74E+13	1.23
1100	1.05E+13	9.95E+12	2.04E+13	1.06
1200	1.16E+13	1.25E+13	2.40E+13	0.93
1300	1.28E+13	1.54E+13	2.81E+13	0.83

### Conclusions

The reaction of tetrahydrofuran (THF) with hydroxyl radicals (OH) has been investigated both experimentally and theoretically in the temperature range of 802-1338 K. The reaction can proceed either via direct or indirect abstraction pathways. Measured rate coefficients agree well with canonical transition state theory calculations. Mutual competition of the two possible H-abstraction channels from THF at the temperature range of this study is also projected.

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# DEVELOPMENT OF AN ETHANOL COMBUSTION MECHANISM BASED ON A HIERARCHICAL OPTIMIZATION APPROACH

Carsten Olm<sup>\*,1,2,3</sup>, Tamás Varga<sup>1,2</sup>, Éva Valkó<sup>1,2</sup>, Sandra Hartl<sup>3</sup>, Christian Hasse<sup>3</sup>, Tamás Turányi<sup>1</sup> <sup>1</sup> Laboratory for Chemical Kinetics, Eötvös University (ELTE), Budapest, Hungary <sup>2</sup> MTA-ELTE Research Group on Complex Chemical Systems, Budapest, Hungary <sup>3</sup> Chair of Numerical Thermo-Fluid Dynamics, TU Bergakademie Freiberg, Freiberg, Germany

# Abstract

A detailed multi-purpose reaction mechanism for ethanol combustion was developed for the use in high-fidelity numerical simulations describing ignition, flame propagation and species concentration profiles with high accuracy. Justified by prior analysis, an optimization of 44 Arrhenius parameters of 14 crucial elementary reactions using several thousand direct and indirect measurement data points was performed, starting from the ethanol combustion mechanism of Saxena and Williams (2007). The optimized mechanism was compared to 13 reaction mechanisms frequently used in ethanol combustion with respect to the reproduction of experimental data.

#### Keywords

Ethanol combustion, Detailed kinetic mechanisms, Mechanism optimization, Parameter uncertainty.

#### Introduction

Ethanol is a widely used renewable alternative fuel and gasoline additive. In the last decade, a considerable growth in the production of fuel ethanol was observed, with the U.S. being the most notable producer, followed by Brazil, EU and China (RFA, 2014). In spite of the widespread use of ethanol in automotive engines, not all details of its combustion chemistry seem fully understood. Describing the combustion kinetics of ethanol with higher accuracy has scientific and practical significance, and can contribute to the development of more efficient car engines with lower pollutant emissions.

The aim of this work is to develop a robust and well-performing detailed mechanism for ethanol combustion following a hierarchical optimization approach. This has two implications: First, the developed mechanism should be "backwards-compatible" and describe smaller combustion systems such as hydrogen and syngas accurately. Second, the optimization targets together with the reactions to be optimized shall be included in a step-by-step strategy, which can accelerate the convergence towards the optimal set of rate parameters.

# Collection of indirect experimental data

A large amount of experimental work has been published on ethanol combustion. Laminar burning velocities were measured in spherical bombs (479 data points/70 datasets), heat flux burners (423/38, including acetylene flames: 54/5) or using the counterflow twinflame technique (89/4). These literature data cover preheat temperatures of 298–500 K, initial pressures of 0.9– 13.8 atm and equivalence ratios of  $\varphi = 0.55$ –1.82. All measurements of laminar burning velocities were carried out with (dry or wet) air, with a few exceptions (measurements in Ar or  $CO_2$  dilution with pure  $O_2$ ).

Ignition delay times were measured in shock tubes (444/39), either using Ar and Ne/Ar ( $\varphi = 0.25-2$ , conditions behind the reflected shock wave:  $p_5 = 0.17-16.9$  atm,  $T_5 = 980-2222$  K) or air ( $\varphi = 0.3-2.0$ ,  $p_5 = 8.9-91.5$  atm,  $T_5 = 778-1570$  K) as diluents. Time-to-ignition data measured in a rapid compression machine (RCM) were also used (20/3;  $\varphi = 0.3$ ,  $T_c = 831-983$  K,  $p_c = 10-50$  bar).

Furthermore, a large variety of concentration profiles were recorded in a wide range of conditions ( $\varphi$ = 0.03–5, p = 1–12 atm, T = 760–1700 K). Concentration–time profiles were measured in flow reactors (1322/14) and shock tubes (8871/14), while outlet concentrations were measured using jet-stirred reactors (593/9) and in flow reactors (459/10). Only major species were considered here (C<sub>2</sub>H<sub>5</sub>OH, O<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, m/z = 28) and each species was counted as separate data point. Fuel was mainly pure ethanol, a few measurements with mixtures of C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>5</sub>OH and pure C<sub>2</sub>H<sub>2</sub> were included as well.

A database for ethanol combustion was created from these experimental data, which was used in the optimization and to compare the mechanisms. Some experimental data were not or could not be used in the present work, e.g. because they were inconsistent with all other collected data or necessary metadata were missing.

# The base mechanism and reactions to be optimized

The mechanism of Saxena and Williams (2007) was chosen based on its overall good performance in predicting the measured data. The  $H_2/CO$  core of the

<sup>\*</sup> Corresponding author: <u>olm@caesar.elte.hu</u>

original mechanism (reactions 1 to 30) was replaced by the optimized syngas mechanism developed in our earlier work (Varga et al., 2014). The excited radical OH\* and the inert gases Kr and Ne were added to the mechanism. In Saxena and Williams (2007), CH<sub>3</sub>CHO decomposition was defined as pressure-independent and only considering the dominant route to CH<sub>3</sub> and HCO. We followed the suggestion of Sivaramakrishnan et al. (2010) to assume pressure dependence and also added the branch yielding CH<sub>4</sub> and CO. These structural changes already led to an improvement in performance, with just a moderate increase in the mechanism size (49 species/251 reactions compared to 46/235).

A brute-force first-order local sensitivity analysis at the conditions of the indirect experimental data was carried out using the base mechanism. The rate parameters of those  $C_1/C_2$  reactions were selected for optimization that produced high sensitivity coefficients at several conditions. Altogether, 44 Arrhenius parameters of 14 reactions were selected (see Table 1). For reactions R176 and R177, both the high-pressure limit (HPL) and the low-pressure limit (LPL) Arrhenius parameters were optimized. Typically, all three Arrhenius parameters (A, n, E) were optimized. In the case of reactions R60, R176 (LPL only) and R177, two Arrhenius parameters (A and E) were sufficient. Direct measurements of the rate coefficients at conditions relevant in combustion were collected from literature for reactions R104, R176-R180 and R188, and used as additional optimization targets (in total 347 data points in 33 datasets).

### The prior uncertainty domain of the parameters

Global parameter optimization methods require the definition of a domain of uncertainty of the parameters, because the optimal parameter set is sought within this domain. As the aim of the present optimization was to find physically realistic rate parameters, the prior uncertainty domain of rate parameters had to be determined. The method for determining this prior uncertainty domain was described by Nagy et al. (2015) and applied to 22 reactions of the H<sub>2</sub>/CO system. For each elementary reaction investigated, all direct measurements and theoretical determinations of the rate coefficient were collected from the NIST Chemical Kinetics Database (http://kinetics.nist.gov/) and from review articles. On an Arrhenius plot, the temperature dependence of ln k outlines an uncertainty band of the rate coefficient. The distance of the  $k_{\min}$  and  $k_{\max}$  limits from the centerline defines the temperature-dependent uncertainty parameter f(T). The f(T) points were converted to the prior covariance matrix of the Arrhenius parameters for each investigated reaction step (Nagy and Turányi, 2011, Turányi et al., 2012). This covariance matrix characterizes the joint posterior uncertainty domain of the parameters. The widths of these uncertainty bands were used as limiting values for the acceptance of rate coefficients during the optimization. For most reactions, little data from literature were available and constant f values were estimated (Table 1).

#### **Parameter optimization**

The global parameter optimization method applied here has been described in detail by Turányi et al. (2012). Its use has been successfully demonstrated by Varga et al. (2014, 2015). Optimization was carried out using response surfaces for burning velocities and ignition delay times. The optimal set of parameters was obtained by minimizing the following objective function (details can be found in Turányi et al. (2012)):

$$E(\mathbf{p}) = \frac{1}{N} \sum_{i=1}^{N} \frac{1}{N_i} \sum_{j=1}^{N_i} \left( \frac{Y_{ij}^{\text{mod}}(\mathbf{p}) - Y_{ij}^{\text{exp}}}{\sigma(Y_{ij}^{\text{exp}})} \right)^2$$
(1)

The optimization involved the fitting of 44 parameters to several thousand data points, which is a computationally challenging task. Therefore, a systematic hierarchical optimization strategy was devised. In the first optimization step those experimental data were selected as optimization targets that were sensitive only to the parameters of the lowest number of reactions. Then more experimental data and the corresponding influential reactions were added following the same concept.

#### The optimized mechanism

Table 1 presents the optimized values of the rate parameters compared to the original values in Saxena and Williams (2007). Table 2 shows the overall value of the objective function decreased significantly as a result of optimization. The description of the experimental data also improved in all three categories. The covariance matrix of all optimized parameters was calculated. These calculated posterior uncertainty limits can only be meaningful in a temperature range for which combustion data was included in the optimization, (approx. 750 - 2400 K, i.e. 1000 K/ $T \approx 0.42 - 1.33$ ). If at the extremes none of the experimental data is sensitive to a certain reactions, the information content of the respective uncertainty limits can be much lower, yielding much wider uncertainty bands. Nevertheless, the uncertainties of k could be effectively reduced in the whole temperature range of interest for most of the reactions.

#### Comparison to published ethanol mechanisms

In recent years, detailed ethanol combustion mechanisms were published by Kathrotia (2011), Konnov (2009), Leplat et al. (2011), Marinov (1999), Herzler and Naumann (2009) ("RD mech"), the San Diego group (2014), Saxena and Williams (2007) and the Zaragoza group (Esarte et al., 2011). Röhl and Peters (2009) published a reduced ethanol mechanism. Mechanisms employing the PLOG formalism were published by Metcalfe et al. (2013) and the NTUA group (Vourliotakis et al., 2015). These could not be used in the present work due to the lack of a stable CHEMKIN-II implementation. Larger mechanisms also tested against ethanol data include the benzene mechanism released by the UCL group (Dias et al., 2014) as well as

*Table 1. Reactions selected for optimization, the rate parameters in the base mechanism (see text) and the optimized values of the parameters. Units are in cm, mol, K and s. Temperature range for f values: 500–2500 K.* 

No.	Reaction string	$f_{ m prior}$	$f_{ m posterior}$	Aorig	<i>n</i> orig	Eorig	$A_{\mathrm{opt}}$	<b>n</b> opt	$E_{ m opt}$
R60	$CH_3+OH = CH_2(S)+H_2O$	1.0	0.90-1.09	4.000E+13	-	1259.38	6.812E+12	-	1426.51
R63	$CH_3+HO_2 = CH_3O+OH$	1.0	0.69–1.71	5.000E+12	_	0	6.106E+02	2.510	-3294.85
R68 LPL	$H+CH_3+M = CH_4+M$	0.70 - 1.06	0.34-0.63	2.470E+33	-4.760	1227.98	4.163E+34	-5.264	-23.09
R104	$C_2H_4+OH = C_2H_3+H_2O$	0.32-0.73	0.19–0.43	5.530E+05	2.310	1491.53	1.088E+04	2.684	874.59
R116	$C_2H_3+O_2 = CH_2CHO+O$	0.4	0.30-0.81	7.000E+14	-0.611	2648.43	6.138E+04	2.327	547.76
R176 HPL	$C_2H_5OH = CH_3 + CH_2OH$	1.0	0.52-0.73	5.000E+15	_	41268.25	9.415E+28	-4.050	43292.13
R176 LPL	$C_2H_5OH + M = CH_3 + CH_2OH + M$	1.0	0.48-0.62	3.000E+16	_	29189.73	2.969E+17	-	29211.08
<b>R177 HPL</b>	$C_2H_5OH = C_2H_4 + H_2O$	1.0	0.16-0.50	8.000E+13	_	32712.63	3.937E+13	-	33198.31
R177 LPL	$C_2H_5OH{+}M=C_2H_4{+}H_2O{+}M$	1.0	0.41-0.65	1.000E+17	_	27176.65	9.876E+17	-	27173.94
R178	$C_2H_5OH+OH = CH_2CH_2OH+H_2O$	1.0	0.16-0.44	1.810E+11	0.400	360.85	9.419E+23	-3.462	2855.69
R179	$C_2H_5OH+OH = CH_3CHOH+H_2O$	1.0	0.37-1.04	3.090E+10	0.500	-191.24	1.143E+10	0.544	-601.84
R180	$C_2H_5OH+OH = CH_3CH_2O+H_2O$	1.0	0.25 - 0.75	1.050E+10	0.800	360.85	2.991E+06	2.113	878.67
R182	$C_2H_5OH+H = CH_3CHOH+H_2$	1.0	0.34-0.64	2.580E+07	1.600	1424.26	2.278E+27	-4.294	5429.12
R188	$C_2H_5OH+CH_3 = CH_3CHOH+CH_4$	0.4	0.34-0.58	7.280E+02	3.000	4001.01	1.475E+05	2.487	5055.49
R190	$C_2H_5OH+HO_2 = CH_3CHOH+H_2O_2$	1.0	0.07 - 0.24	8.200E+03	2.500	5435.33	2.611E+25	-3.694	10358.18
R196 LPL	$CH_3CH_2O+M = CH_3+CH_2O+M$	0.7	1.04-1.18	5.350E+37	-7.000	11977.86	9.154E+31	-5.484	10738.93

*Table 2. Comparison of error function values by experiment type and overall between 13 published mechanisms, the base mechanism for optimization (see text) and the new optimized mechanism. CHEMKIN-II solvers were used.* 

Mechanism ID	Ignition delay times	Burning velocities	Major species profiles	Overall
Kathrotia-2011*	195.6	-	357.2	-
Konnov-2009	82.2	-	1179.9	_
Leplat-2010	37.9	6.3	116.2	37.1
Marinov-1999	62.5	-	109.2	_
RDmech-2009	58.5	32.6	1272.5	313.9
RöhlPeters-2009	60.5	8.1	96.0	38.1
SanDiego-2014	20.1	45.1	5019.8	1148.2
SaxenaWilliams-2007	49.1	17.2	248.7	75.1
Zaragoza-2011	45.1	_	133.1	_
DagautTogbé-2012*	46.6	-	89.7	_
Ogura-2007	68.2	-	105.3	-
UCL44f-2013	52.2	-	215.4	_
ZhongZheng-2013**	97.0	7.5	915.4	227.5
Base mechanism	42.7	9.8	146.4	46.8
New optimized mechanism	<b>9.8</b> (1 <sup>st</sup> )	<b>6.3</b> (2 <sup>nd</sup> )	<b>63.5</b> (1 <sup>st</sup> )	<b>20.0</b> (1 <sup>st</sup> )
No. of data points	42	122	47	211
No. of datasets	464	991	11245	12700

For 1D simulations, species with  $\geq$  4 C atoms were removed, together with all reactions in which they participate.

\*\* In shock tube simulations, dp/dt was chosen as an ignition criterion wherever necessary, as the CH radical is not defined in the mechanism. For 1D simulations, species with  $\ge 6$  C atoms were removed, together with all reactions in which they participate.



Figure 1. Selected Arrhenius plots with the initial and optimized rate coefficients, and prior and posterior uncertainties.

the iso-octane mechanisms of Dagaut and Togbé (2012), Ogura et al. (2007) and Zhong and Zheng (2013).

While only ranked a close 2<sup>nd</sup> for laminar burning velocities among the investigated mechanisms, the major strength of the newly optimized mechanism is its improved accuracy in 0D simulations. Overall, it is by far the best mechanism in the present comparison.

# Conclusions

The present article demonstrates the optimization of a detailed ethanol combustion mechanism starting from Saxena and Williams (2007). A large amount of experimental data was collected from the literature including ignition delay times, burning velocities, concentration profiles and direct measurements of rate coefficients. As a results of local sensitivity analysis, 44 Arrhenius parameters of 14 elementary reactions were identified and subsequently optimized. Direct measurements and theoretical determinations related to these reactions were used to outline the prior uncertainty domain of the rate coefficients. The optimization provided optimized values for all parameters as well as posterior uncertainty bands for the rate coefficients. The performance of the optimized mechanism was compared with those of several published mechanisms. It was shown that the optimized mechanism clearly provides the overall best description of the currently available experimental data, while the optimized rate coefficients are consistent with the respective direct measurements and literature values.

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# SURFACE REACTION KINETICS OF STEAM- AND CO<sub>2</sub>-REFORMING AS WELL AS OXIDATION OF METHANE OVER Ni, Rh, Pt-BASED CATALYSTS

Lubow Maier<sup>1</sup>, Karla Herrera Delgado<sup>1</sup>, Lea Kahle<sup>2</sup>, Canan Karakaya<sup>3</sup> and Olaf Deutschmann<sup>1\*</sup> <sup>1</sup>Karlsruhe Institute of Technology (KIT), D-76131Karlsruhe/Germany; <sup>2</sup>Cargill GmbH, 55120 Mainz/Germany; <sup>3</sup>Colorado School of Mines, Golden, CO 80401/USA

#### Abstract

An experimental and kinetic modeling study on Ni, Rh, and Pt-catalyzed reactions of methane under oxidative and reforming conditions is presented. Using the experimentally determined conversion in steam and dry reforming as well as partial oxidation of CH4 over a catalytically coated disk, honeycomb monolith, and powdered backed bed catalyst a thermodynamically consistent multi-step reaction mechanisms with the associated rate expressions were developed. All the experimental configurations were numerically simulated coupling models for the flow field with these heterogeneous reaction mechanisms. Elementary-step surface kinetics were developed using the mean-field approximation, including adsorption and surface reactions of methane with oxygen, steam, and CO<sub>2</sub> as well as water-gas shift reaction, methanation, and surface carbon formation. Kinetic parameters of reversible elementary steps were derived from transition-state theory and semi-empirical methods. Comparative sensitivity and flow analysis of reaction paths are caried out at the different operating conditions over catalysts studied. Ni-, Rh-, and Pt- surface kinetic models developed allow for prediction of conversions, selectivities, ignition temperatures, and concentrations profiles for a wide range of mixture composition, contact time, and temperature.

#### Keywords

Catalytic methane reforming, Nickel, Rhodium, Platinum, Surface reaction mechanism

# Introduction

The synthesis gas generation from natural gas (methane), as alternative to conversion of refinery offgases, naphta, and coal, draws recently a renewed attention in both academic and industrial research due to the increment of fossil fuels prices and the environmental problems derived from useful energy generation sources. A major step in gas-to-liquid (GTL) technologies is conversion of CH<sub>4</sub> to synthesis gas (a mixture of H<sub>2</sub> and CO) via catalytic partial oxidation (CPOX), steam reforming (SR), dry reforming (DR) processes, and their combinations. Produced synthesis gas is an usual feed stock for ammonia/urea synthesis, oil refining operations, and for production of synthetic liquid fuels such as methanol and liquid hydrocarbons by Fisher-Tropsch synthesis (Rostrup-Nielsen et al., 2002). Hydrogen separated from the synthesis gas is progressivly used for on board or stationary power generation by fuel cell applications or in conventional vehicles internal engines to decrease the pollutant emissions during the cold start-up (Kaltschmitt and Deutscmann, 2012). Noble metals Rh and Pt es well es non-noble metalbased catalysts such es Ni, dispersed on a support material (Al<sub>2</sub>O<sub>3</sub>, MgO, ZrO<sub>2</sub>), are efficiently used for partial oxidation and reforming of CH<sub>4</sub> in large-scale commercial applications.

There are many factors, including catalyst type, operating conditions and reformer design

features, which influence the performance of the reforming process and product distribution. Therefore, it is important to contribute a fundamental understanding of the reaction mechanisms over the catalysts and reveal the complex interaction beetwin the catalyst surface and ambient gas mixture at the molecular level. Understanding and optimization of these processes can be facilitated by the use of detailed computational models that incorporate elementary reaction mechanisms (Deutschmann, 2007). The development of such detailed mechanism-based models offers the possibility of predictive kinetics models providing the information about the governing chemistry and reactor behavior. The models are especially required for the analysis and optimization of the catalyst composition, operating conditions and reactor design.

The objective of this work is the development of the multi-step surface reaction mechanisms for catalytic conversion of methane over Pt, Rh, and Ni, catalysts under oxidative and reforming conditions and their comparative analysis over a wide range of operating conditions in different experimental set-ups.

#### **Modeling Approach**

The numerical model is based on the detailed surface reaction mechanisms, which are implemented

in a one-, and two-dimensional flow field descriptions of a stagnation-flow reactor (SFR), packed bed reactor (PBR), and tubular flow reactor with appropriate models for mass and heat transport. All computational simulations were performed by using DETCHEM<sup>TM</sup> (Deutschmann et al., 2013) software.

The mean-field approximation is applied to describe the Langmuir-Hinshelwood like reactions (Deutschmann, 2007). The state of the catalytic surface is described by the temperature T and a set of surface coverages  $\theta_i$ . The surface temperature and the coverages depend on time and the macroscopic position in the reactor, but are averaged over microscopic local fluctuations. Under those assumptions the molar net production rate  $\dot{s}_i$  of a chemical species i on the catalyst is given as:

$$\dot{s}_{i} = \sum_{k=1}^{K_{s}} v_{ik} k_{ik} \prod_{j=1}^{N_{g}+N_{s}} c_{j}^{\nu' jk}$$
(1)

where  $k_{fk}$  describes the rate coefficients of  $K_s$  surface reactions among  $N_g$  gas-phase and  $N_s$  surface species. The concentrations  $c_j$  of adsorbed species are given in mol/m<sup>2</sup>. The dynamics of the locally varying surface coverage of adsorbed species  $\theta_j$ , is determined by:

$$\frac{\partial \theta_i}{\partial t} = \frac{\sigma_i \dot{s}_i}{\Gamma}$$
(2)

here,  $\sigma_i$  indicates the number of surface sites, that are occupied by species *i*,  $\Gamma$  is the surface site density, i.e., the number of adsorption sites per catalytic surface area, that can be calculated from the catalyst material. The values of 2.77 $\cdot 10^{-9}$ , 2.60 $\cdot 10^{-9}$ , and 2.72 $\cdot 10^{-9}$ mol/cm<sup>2</sup> were used for Rh, Ni, and Pt respectively.

Since the binding states of adsorption of species vary with the surface coverage, the extended expression for the rate coefficient is used (Deutschmann et al., 2013):

$$k_{f_k} = A_k T^{\beta_k} \exp\left[\frac{-E_{ak}}{RT}\right]_{i=1}^{N_k} \theta_i^{\mu_{ik}} \exp\left[\frac{\varepsilon_{ik}\theta_i}{RT}\right]$$
(3)

At steady-state Eq. (2) become a set of coupled, nonlinear algebraic equations. The following boundary condition applies for the flux  $j_i$  at the catalyst surface in steady-state:

$$j_{i,surf} = j_i + \rho Y_i v_{st} = F_{cat/geo} \cdot \eta M_i \dot{s}_i, \qquad (4)$$

where  $j_{i,surf}$  is the diffusive mass flux at the surface,  $v_{st}$  is the Stefan velocity, and  $F_{cat/geo}$  the ratio between the catalytically active surface area and geometric surface area, that can be determined experimentally, e.g. by chemisorption measurements. The effect of internal mass transfer resistance for catalyst dispersed in a porous media is included by the effectiveness factor  $\eta$ .

Detailed heterogeneous reaction kinetics include gas-phase species (CH<sub>4</sub>, O<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O) and surface intermediates (CH<sub>4</sub>\*, CH<sub>3</sub>\*, CH<sub>2</sub>\*, CH\*, C\*, O\*, OH\*, CO\*, CO<sub>2</sub>\*, H\*, HCO\*, HCOO\*, COOH\*, H<sub>2</sub>O\*). Kinetic parameters of reversible elementary steps were derived from transition-state theory and semi-empirical UBI-QEP method (Shustorovich, 1990) for the Rh(111), Pt(111), and Ni(111) surfaces in the limit of zero coverage. Selected steps were corrected for coverage dependent activation energies. Lately developed optimization procedures have been applied to ensure overall thermodynamic consistency (Maier et al., 2011; Herrera Delgado et al., 2015).

#### **Results and Discussion**

Experiments and numerical simulations are conducted by following a hierarchical methodology, i.e., the complexity of the reaction kinetics was stepwise increased starting from  $H_2$  and CO catalytic combustion, via preferential oxidation of CO with  $H_2$ co-feed, water-gas shift (WGS) and reverse water-gas shift (RWGS) reactions and ending up with partial oxidation, steam reforming, and dry reforming of CH4.

Figures 1, 2, and 3a compare model predictions with experimental data and gives the examples of how well the models are capable of describing CPOX, SR, DR, WGS and RWGS integral data in different experimental set-ups.

The water-gas shift reaction is one of the crucial reactions that determine the overall product selectivity in methane conversion by CPOX, SR, and DR. WGS reaction mechanism was studied experimentally and numerically by stagnation-flow technique over Ni/Al2O3 and Rh/Al2O3 coated disk (Karakaya et a., 2014), in tubular flow reactor with Rh (Karakaya et al, 2014), and Pt (Kahle et al, 2013) coated honeycomb monolith. Figure 1 shows the comparison of model predicted and the experimentally measured data for WGS (a) and RWGS (b) reactions over Pt. Kinetic modeling studies with the developed detailed reaction mechanisms reveal that WGS over Pt mostly follows the redox or formate pathways via interaction of CO\* with O\* forming CO2\* or OH\* forming HCOO\*, respectively, depending from operating conditions. However, the formation of carboxyl species COOH\* is the dominant pathway for WGS and RWGS over rhodium und nickel.

CPOX, SR, and DR reaction mechanisms were studied experimentally using SFR over  $Rh/Al_2O_3$  (Karakaya et al, 2012) and PBR over  $Ni/Al_2O_3$  (Herrera Delgado et al., 2015) catalysts.

Fig 2a shows the experimentally measured species concentrations in comparison with the numerical predictions as a function of the temperature



Figure 1. Comparison of the experimentally measured (symbols) and numerically simulated (line) mole fractions of products during the WGS reaction for a CO/H<sub>2</sub>O ratio 1 (a) and RWGS reaction for a CO<sub>2</sub>/H<sub>2</sub> ratio of 10 (b) in 94% N2 dilution at the 10 mm long Pt-coated 400 cpsi monolithic catalyst at inlet flow rate of  $6.7e^{-5}$  m<sup>3</sup>/s.

for catalytic partial oxidation of methane in a fixed bed reactor over Ni/Al2O3 catalyst (Herrera Delgado et al., 2015). At low temperatures (up to 880 K), O<sub>2</sub> is converted and deep oxidation occurs (CO2 and H2O are the main products); at higher temperature, where  $O_2$  is compeletly converted, syngas is produced, and steam and CO<sub>2</sub> are being consumed. The data show methane steam and dry reforming at high temperature, i.e., the indirect route to syngas. The computed concentrations of the gas-phase species along the catalytic bed (Fig 2b) and surface coverage of species (Fig 2c) at 973 K after ignition support the indirect route of H<sub>2</sub> and CO formation. Syngas is produced through steam and some dry reforming of methane after 14 mm downstream the catalyst bed, where oxygen is comletely consumed. The species OH\* and H<sub>2</sub>O\* observed have a maximum concentration on the surface at the axial position of 14 mm (not shown).

All developed surface reaction mechanisms include two possible pathways for catalytic activation of methane: via oxidative dehydrogenation ( $CH^*_x + O^*$  $\rightarrow CH^*_{x-1} + OH^*$ ) and pyrolytic path ( $CH^*_x + *$  $\rightarrow CH^*_{x-1} + H^*$ ). Reaction flow analysis performed for different catalysts reveals that partial oxidation over Pt, Rh, and Ni follows the oxygen assisted dehydrogenation, whereas the pyrolytic path is dominant for SR and DR.

Figure 3 shows an example of experimental and kinetic modeling study of methane SR and DR in

stagnation flow reactor over Rh catalyst (Karakaya et



Figure 2. Concentrations of products as a function of temperature (a), axial profiles of gas-phase species (b), and surface coverages (c) at 973K for catalytic partial oxidation of methane in a backed bed reactor over Ni/Al<sub>2</sub>O<sub>3</sub> catalyst: CH<sub>4</sub>/O<sub>2</sub> = 1.6 in 97% N<sub>2</sub>; 1 bar;  $T_{inlet}$ = 373 K; total flow rate of 4 slpm; symbols: experimental data; solid lines: model prediction.

al., 2012).

The sensitivity and reaction flow analyses were performed to examine dominant reaction pathways and rate determining steps for the catalysts studied in this work at the different operating conditions. Figure 4 shows comparative reaction path analysis for methane SR and DR over Ni, Rh, und Pt. The both reactions indicate the pyrolytic path of methane activation. The following CO oxidation over Ni and Rh proceeds through the formation of carboxyl species (COOH\*) in the reaction with OH\*, whereas the direct oxidation with surface O\*, produced via dissociative adsorption of H<sub>2</sub>O or CO<sub>2</sub>, is the main path for Pt. The results of sensitivity analysis reveal that, the rate-determining steps for all three metals are the adsorption and the dehydrogenation of CH<sub>4</sub>. The reaction of SR at moderate and low temperature

regimes is sensitive to the formation of carboxyl species over Rh and Ni while the direct reaction of  $CO^* + OH^*$  to  $CO_2$  become sensitive over Pt.



Figure 3. Species mole fractions along the boundary-layer for steam reforming of CH<sub>4</sub>, S/C=1.06, 973K (a) and dry reforming of CH<sub>4</sub>,  $CH_4/CO_2=0.66$  in 75% Ar at 1073K (b) in the SFR over 5% Rh/Al<sub>2</sub>O<sub>3</sub> catalyst; symbols: experimental data; solid lines: model prediction



Figure 4. Reaction flow analysis for steam and dry reforming of methane ( $CH_4/H_2O$ ,  $CH_4/CO_2$  ratio of 0.9 in 70% Ar) at 973K over Ni, Rh (a), and Pt catalysts (b), \* implies an adsorbed species.

# Conclusions

The kinetics of oxidation and reforming of methane over Pt, Rh, and Ni were studied experimentally and numerically, based on experimental studies of partial oxidation as well as dry and steam reforming of methane performed in stagnation-flow reactor, in tubular flow reactor with catalytic honeycomb monolith, and in a packed bed reactor under varying conditions. The detailed reaction mechanisms for the catalytic conversion of methane under oxidative and reforming conditions were developed and evaluated by comparison of experimentally derived and numerically predicted conversion and selectivity. The mechanisms were implemented into in a one-, and two-dimensional flow field descriptions of the appropriate reactor configurations.

The models developed can be extended for industrial applications, quantitatively predicting the effect of inlet compositions, operating conditions and reactor design.

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## CO<sub>2</sub> Methanation: Catalyst Synthesis and Kinetics

F. Koschany, D. Schlereth, O. Hinrichsen,

Technische Universität München, Department of Chemistry, Lichtenbergstraße 4,85748 Garching b. München, Germany Technische Universität München, Catalysis Research Center, Ernst-Otto-Fischer-Straße 1, 85748 Garching b. München, Germany

Keywords: Methanation, Kinetics, CO<sub>2</sub>, Nickel

#### Introduction

Due to the fluctuation of renewable energy supply by wind and solar power stations, research in the field of power storage systems is required more than ever. Methane, which can be synthesized by the methanation of waste  $CO_2$  and  $H_2$ , e.g. from electrolysis, will function as potential chemical energy storage. For  $CO_2$  methanation several metal catalysts, e.g. Rh, Ru, Pd and Ni have been tested and potential reaction mechanisms have been proposed [2,3]. In our research group, different Ni/Al<sub>2</sub>O<sub>3</sub> catalysts were synthesized, characterized and the kinetics of the  $CO_2$  methanation were investigated.

#### **Experimental Work**

Nickel-Alumina catalysts with different Ni/Al ratios between 1/5 and 5/1 were synthesized by co-precipitation [4]. Catalysts were characterized by BET, chemisorption and XRD. For comparison of the catalytic activity, the specific  $CO_2$  conversion was determined stepwise in the temperature range between 175 and 500°C and detailed kinetic measurements were conducted. The kinetic data pool is recorded in the temperature range from 180 to 350°C and a pressure range from 1-13 bar.

#### Results

The expected Ni/Al ratio of the synthesized catalysts was confirmed by quantitative elemental analysis. The BET surface area is between 230-150 m<sup>2</sup>/g, decreasing with higher Ni content. The specific Ni surface area increases with higher Ni loadings and is linear correlated to the catalysts activity as shown in Fig. 1. Based on a Langmuir-Hinshelwood-Hougen-Watson mechanism a rate equation was derived from the kinetic data pool. By varying temperatures and feed composition, apparent activation energy and reaction order are assessed. Compared to the experimental data in Fig.2, a good agreement with the average absolute residual being 6.8% was obtained.

#### **Conclusion and Outlook**

In this study a kinetic model was derived, describing the catalysts activity over a wide range of industrially relevant reaction conditions. In upcoming experiments we will promote our Ni/Al systems with different other metals. An additional focus will be set on identification of structure activity relations to gain a deeper understanding of the catalyst system.

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Figure 1: Correlation between WTY and specific Ni surface area.



Figure 2: Parity plot for calculated and measured reaction rates.

## The Critical Role of Water in Catalytic CO oxidation over Au/TiO<sub>2</sub> Catalysts

L. C. Grabow<sup>1,\*</sup>, J. Saavedra<sup>2</sup>, H. A. Doan<sup>1</sup>, C. J. Pursell<sup>2</sup> and B. D. Chandler<sup>2</sup> <sup>1</sup>University of Houston, Houston, TX 77019 <sup>2</sup>Trinity University, San Antonio, TX, 78212

Keywords

CO Oxidation, DFT, gold, titania, kinetic isotope effect

When it comes to chemical properties, gold is known to be inert. That is, until Haruta and coworkers discovered the high catalytic activity of supported Au nanoparticles, which enables CO oxidation to occur even below room temperature.<sup>1</sup> Concomitantly, the presence of water in the reaction has been found to significantly increase the rates of CO<sub>2</sub> formation.<sup>2</sup> The discovery has led to extensive research aiming at elucidating the reaction mechanism and the nature of the active sites. Recent advancements established that the low-coordinated, peripheral sites around Au nanoparticles are the reaction sites for CO oxidation.<sup>3,4</sup> However, no consensus has been reached in regard of the promotional effects of water as well as its role in the mechanism. Here, we use kinetic measurements, isotopic labeling, in situ IR spectroscopy, and first-principles simulations to study CO oxidation on Au/TiO<sub>2</sub>, and our results provide direct evidence for a novel water-mediated reaction mechanism.<sup>5</sup> A hydrogen/deuterium kinetic isotope effect of nearly 2.0 implicates O-H(D) bond breaking in the rate determining step. Kinetics and in situ IR spectroscopy experiments showed that the coverage of weakly adsorbed water on TiO<sub>2</sub> largely determines catalyst activity by changing the number of active sites. Density functional theory calculations indicated that adsorbed water at the metal/support interface acts as a cocatalyst and greatly facilitates oxygen adsorption and activation; the resulting Au-OOH species readily reacts with adsorbed Au-CO, yielding Au-COOH. Subsequent Au-COOH decomposition involves proton transfer to water, and was suggested to be the rate-determining step. These experimental and theoretical results provide a fresh framework for interpreting the literature, and clearly define the mechanistic roles of water, support OH groups, and the metalsupport interface.

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## Pt CLUSTERS IN LTA ZEOLITE FOR HYDROGEN COMBUSTION IN HYDROCARBON RICH CONDITIONS

Yu-Ling Shan<sup>1</sup>, Zhi-Jun Sui<sup>1</sup>, De Chen<sup>2</sup> and Xing-Gui Zhou<sup>1,\*</sup> <sup>1</sup>East China University of Science and Technology, Shanghai 200237, P. R. China <sup>2</sup>Norwegian University of Science and Technology, N-7491, Trondheim, Norway \**Corresponding <u>xgzhou@ecust.edu.cn</u>* 

Keywords

Pt encapsulation, LTA zeolite, coke resistant, selective hydrogen combustion.

Propane dehydrogenation has become an important alternative way for on-purpose production of propene, since traditional ways of producing it can no longer meet the ever growing global need. However, this intrinsic highly endothermic process is usually operated at high temperatures to overcome thermodynamic limitations<sup>1</sup>. The concept of autothermal reactor, in which selective hydrogen combustion (SHC) is incorporated, has been proposed to improve the energy efficiency. To this end, the catalysts used should possess the ability of combusting hydrogen with high selectivity under severe conditions, *i.e* high temperature and propene rich atmosphere. However, the currently used Pt catalysts suffer the problem of low selectivity and fast deactivtion<sup>1</sup>.

Herein, the concept of shape selective catalysis is explored based on the differences of interested reactants in molecular size (H<sub>2</sub> (2.8 Å), O<sub>2</sub>(3.5 Å) and C<sub>3</sub>H<sub>8</sub> (4.3 Å), C<sub>3</sub>H<sub>6</sub> (4.5 Å)). It is found that, among LTA zeolites (KA (3A), NaA(4A), CaA(5A)), NaA zeolite with pore size of 4.1 Å is capable of separating these four molecules. Thus, Pt clusters are introduced into these zeolite through direct hydrothermal synthesis method<sup>2</sup>. The obtained solids are characterized by several techniques like XRD, HAADF-STEM and TEM-EDS, and the results show that Pt can be homogenously distributed in zeolites with mean particle size of 1.2 nm, which is similar to the dimension of  $\alpha$  cages of LTA zeolite. The successful encapsulation of Pt clusters is also verified by propane dehydrogenation over these Pt/LTA zeolites.

The performances of these catalysts in SHC were evaluated in presence of propane at 550 °C, the results show that > 99% of oxygen are consumed over all catalysts and Pt/KA shows the highest selectivity to water (99.5% versus 98.9% over PtSn/SiO<sub>2</sub>). The real challenge is to introduce 30% of propene in the feed, under which condition the selectivity of PtSn catalyst drops from 97.2% to 67.5% and the coke content increases to 52.3% in 25 h. Contrarily, the selectivity over Pt/LTA catalysts are higher (94.8% for Pt/KA, 82.0% for Pt/NaA, 76.2% for Pt/CaA) with negligible coke content of 0.46% and 0.70% for Pt/KA and Pt/NaA, respectively. But the oxygen conversion over Pt/LTA catalysts decreases significantly to 30-60%, which is due to the zeolite's affinity to propene that limits the access of oxygen. This problem is solved by further introducing alkali metals like K, Na, Ca and Ba onto these catalysts, and SHC with high activity (oxygen conversion > 92.0%) and selectivity (oxygen to water > 98.5%) are achieved.

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## Assessment of catalytic performance for Oxidative Coupling of Methane via Comprehensive Microkinetic Modelling

V.I.Alexiadis<sup>1</sup>, M. Chaar<sup>2</sup>, A.Van Veen<sup>2</sup>, J.W.Thybaut <sup>1\*</sup>, G.B. Marin<sup>1</sup>, <sup>1</sup>Ghent University, Ghent, Belgium, <sup>2</sup>Ruhr-Universität Bochum, Bochum, Germany

#### Abstract

A comprehensive microkinetic model, that specifically accounts for the homogeneous as well as heterogeneously catalyzed reaction steps in OCM was used in the assessment of large kinetic datasets acquired on five different catalytic materials. By virtue of the included catalyst descriptors the applicability of the model was extended from the class of alkali magnesia catalysts represented by Li/MgO and Sn-Li/MgO and alkaline earth lanthana catalysts represented by Sr/La<sub>2</sub>O<sub>3</sub> to rare earth-promoted alkaline earth calcium oxide catalysts, represented by LaSr/CaO, and a Na-Mn-W/SiO<sub>2</sub> catalyst. The model succeeded in adequately simulating the performance of all five investigated catalysts in terms of reactant conversión and product selectivities in the entire range of experimental conditions. It was found that the activity of Sr/La<sub>2</sub>O<sub>3</sub>, in terms of methane conversion, is approximately 2, 5, 30 and 33 times higher than over the La-Sr/CaO, Sn-Li/MgO, Na-Mn-W/SiO<sub>2</sub> and Li/MgO catalysts, respectively, under identical operating conditions. This was attributed mainly to the high stability of adsorbed hydroxyl species, the high stability of adsorbed oxygen and the high active site density on Sr/La<sub>2</sub>O<sub>3</sub>. The selectivity towards C<sub>2</sub> products was found to particularly depend on the methyl radical sticking coefficient and the stability of the adsorbed oxygen and was the highest on the Na-W-Mn/SiO<sub>2</sub> catalyst, i.e., 75% at about 1% methane conversion at 1023 K, 190 kPa and inlet molar CH<sub>4</sub>/O<sub>2</sub> ratio of 4.

#### Keywords

Oxidative coupling of methane, Ethylene, catalyst descriptors, microkinetic modelling

#### 1. Introduction

Oxidative coupling of methane (OCM) to ethane and particularly ethylene has been studied for more than 30 years (Keller and Bhasin, 1982) and offers great industrial potential, since it could broaden the feedstock basis for chemical industry (Mleczko, 1995). OCM can be described as a gas phase reaction which is initiated via a heterogeneous catalyst. The catalyst is activated through reversible dissociative oxygen chemisorption and subsequently produces gas phase methyl radicals by hydrogen abstraction from methane. The formed methyl radicals either couple in the gas phase to form  $C_2$  products or are oxidized towards carbon oxides (Couwenberg et al., Alexiadis et al., 2014, Sun et al., 2008). An elaborate microkinetic model for OCM that includes catalyst descriptors and accounts for thermal, homogeneous, and catalytic, heterogeneous, reaction steps has been developed to be employed for the fine tuning on the best catalytic materials. Model parameters such as reaction enthalpies and activation energies have been related to selected chemisorption enthalpies. The latter are denoted as catalyst descriptors and the established relationships between these descriptors and the model parameters have been constructed to be valid for an entire catalyst library. A more detailed description of the OCM microkinetic model is presented by Kechagiopoulos et al. (2014). The recent study of Alexiadis et al. (2014) focuses on the ability of the

In the present work, the developed model is employed to investigate the performance of catalysts, representative of two morecatalyst families, i.e., rare earth-promoted alkaline earth calcium oxide catalysts, represented by LaSr/CaO and NaMnW/SiO2 catalysts, and provide an unequivocal comparison of their OCM behavior with that of the lithium magnesia and the alkaline earth lanthana catalysts. The implementation of the microkinetic model on a series of catalysts belonging to the same family is rather straightforward, yet a similar effort for catalysts belonging to various families is significantly more challenging.

#### 2. Procedures

#### 2.1 Experimental

Extensive OCM experimental data sets have been acquired over a 10%La-20%Sr/CaO and a 1wt%Na-3%W-2%Mn/SiO<sub>2</sub> catalyst over a wide range of operating conditions. It has been reported that CaO is a high temperature, stable, basic catalyst support with La being involved in the oxygen activation and Sr enhancing the C<sub>2</sub> selecticity. The composition as used in the present work, i.e., 10%La – 20%Sr/ CaO, follows from an earlier screening [Olivier et al., 2008,

model to assess OCM kinetic data acquired on catalysts that are representative of two different classes of materials, i.e., lithium magnesia and alkaline earthpromoted lanthana catalysts, and associate their performance in terms of methane activation and C2 selectivity to selected catalyst descriptors.

<sup>\*</sup> To whom correspondence should be addressed Joris.Thybaut@UGent.be

Thybaut et al., 2011). NaWMn/SiO<sub>2</sub> catalysts have been investigated extensively for OCM . It has been reported that these catalysts present a remarkable stability under the high temperatures as required for OCM (Arndt et al., 2012, Wang et al., 2006, Zheng et al., 2010). Hence, within the current investigation, a catalyst with composition 1wt%Na-3%W-2%Mn/SiO2 was studied, identical to a literature reported catalyst, in terms of preparation method and composition (Wang et al., 2006).

The experimental data over LaSr/CaO and NaMnW/SiO<sub>2</sub> were produced in a fixed bed reactor. Further information on the set-up can be found elsewhere (Alexiadis et al., 2014). The reproducibility of the kinetic measurements was ensured by applying a standardized lining-out pretreatment for both catalysts, identical to the one previously applied for Sr/La<sub>2</sub>O<sub>3</sub> catalyst (Alexiadis et al., 2014). Extensive kinetic datasets were compiled over LaSr/CaO and NaMnW/SiO<sub>2</sub> catalysts comprising 157 and 228 observations respectively.

#### 2.2 Modelling

The OCM microkinetic model was in the first instance validated against the experimental data produced over the LaSr/CaO and the NaMnW catalysts. An elaborate description of the model has been reported elsewhere (Kechagiopoulos et al., 2014, Alexiadis et al., 2014).

In a nutshell, the set of catalyst descriptors in the OCM microkinetic model can be classified as follows :

- a) Hydrogen abstraction reaction enthalpy from  $CH_4(D_1)$
- b) Chemisorption heats of O<sub>2</sub>, CH<sub>2</sub>O, HCO, CO, CO<sub>2</sub>, H<sub>2</sub>O, C<sub>2</sub>H<sub>4</sub>O, C<sub>2</sub>H<sub>3</sub>O (D<sub>2</sub>-D<sub>9</sub>)
- c) Initial sticking probabilities of O<sub>2</sub>, CH<sub>3</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, C<sub>2</sub>H<sub>4</sub> (D<sub>10</sub> D<sub>15</sub>)
- d) Density of active sites  $(D_{16})$

#### 3. Results and discussion

## 3.1 Comparison of the observed OCM behaviour of the investigated catalysts

Performances of the aforementioned five catalysts were compared in terms of methane conversion and  $C_2$ selectivity. Representative experimental results showed that Li/MgO and NaMnW/SiO<sub>2</sub> are, by far, the least active catalysts. Sr/La<sub>2</sub>O<sub>3</sub> appeared to be more active and slightly less selective than LaSr/CaO at roughly similar reaction conditions. The experiments with the SnLi/MgO catalyst were carried out at much more concentrated conditions, higher space times and slightly lower CH<sub>4</sub>/O<sub>2</sub> ratio, which are all expected to promote methane conversion.

#### 3.2 Model validation/regression analysis

The experimental data produced over LaSr/CaO and NaMnW/SiO2 catalysts were simulated by employing the OCM microkinetic model in order to assess the distinct activity and selectivity patterns in the performance of these two investigated catalysts. As reported in our previous work (Alexiadis et al., 2014)

the model is most sensitive to the following four catalyst descriptors:  $D_1$ ,  $D_2$ , D11 and  $D_{16}$ . During the regression analysis, only these descriptors were allowed to vary. The values of the remaining catalyst and kinetic descriptors, were fixed at the values obtained, during the preliminary parameter estimation performed over the Sr/La<sub>2</sub>O<sub>3</sub> data (Alexiadis et al., 2014).

Reduced data sets of 36 and 43 experiments for LaSr/CaO and NaMnW/SiO2 catalyst respectively were used during parameter estimation to minimize the computational time. The so obtained parameter estimates were subsequently employed for the simulation of all 157 and 228 observations on LaSr/CaO and NaMnW/SiO<sub>2</sub> respectively. The microkinetic model yielded a very good agreement with the experimental data in terms of conversions, selectivities and outlet molar fractions of the various components for the complete range of experimental conditions over each of the two catalysts despite the limited number of adjustable parameters. The adequate agreement between calculated and experimental data had been also observed in the case of the other three catalysts (Alexiadis et al., 2014). Table 1 presents the estimates for the adjustable catalyst descriptors for all the investigated catalysts. The high F value for the global significance of the regression of 871.1 illustrates the model's conformity to the experimental data.

# 3.2.1 Interpretation and quantification of the experimental differences

As elaborately described in our previous work (Alexiadis et al., 2014) the methane hydrogen abstraction reaction enthalpy,  $D_1$ , is related to the chemisorption enthalpy of OH- species. Comparison of the D<sub>1</sub> estimates reported in Table 1, pertaining to the five investigated catalysts, shows that this step is highly endothermic in the case of LiMgO as well as the NaMnW/SiO<sub>2</sub> catalyst. This, in essence, means that hydroxyls are less stable on these catalysts, i.e., their chemisorption heat is relatively low and, within the range of the catalyst descriptor values presented in Table 1, this was found to lead to a decrease of catalytic methane conversion. The positive difference in the activation energies between the forward and the reverse methane hydrogen abstraction step increases with the endothermicity, slowing down methane the overall conversion. Furthermore, the active site density  $(D_{16})$  on these two catalysts is much lower than in the case of Sr/La2O3, LaSr/CaO and SnLi/MgO catalysts, implying the limited contribution of the catalytic reactions to the overall OCM reaction over NaMnW/SiO<sub>2</sub> and LiMgO. These findings reveal the intrinsic reason for the low activity of NaMnW/SiO2 and LiMgO catalysts, mentioned in section 3.1.

Further analysis of the catalyst descriptor estimates presented in Table 1 can give an additional reason for the low activity, yet simultaneously the high selectivity attained to C2 products with the NaMnW/SiO<sub>2</sub> catalyst.

Table 1. Estimates for the catalyst descriptors pertaining to the five investigated catalysts

	Catalyst descriptor	Unit	LaSr/CaO	NaMnW/SiO <sub>2</sub>	Sr/La <sub>2</sub> O <sub>3</sub>	Li/MgO	SnLi/MgO
$D_1$	Reaction enthalpy of	(kJ mol <sup>-1</sup> )	65.1±1.6	81.4±0.002	$44.4\pm0.2$	91.2±0.2	56.6±0.8
	hydrogen abstraction from						
	CH.						
D		(1 T 1-1)	120 6 5 2	11.10	110 5 . 2 5	72 ( . 2.2	(0.54.0.C
$D_2$	Chemisorption heat of $O_2$	(KJ mol <sup>-</sup> )	139.6±5.3	44±1.0	119.5±3.5	/3.6±2.2	60.54±2.6
D.,	Initial sticking probability		1 14+0 03 10-4	$1+0.2 \ 10^{-5}$	$6.49 \pm 0.5 10^{-4}$	1 19+0 0002 10-4	6 22+0 1 10 <sup>-5</sup>
DII	-f CU -		1.14±0.05 10	1±0.2 10	0.47 ±0.5 10	1.19±0.0002 10	0.22±0.1 10
	of CH <sub>3</sub> .	( )	5 4 4 <del>5</del> 406		0.04 4.406		1 22 0 02 10 6
$D_{16}$	Density of active sites	(mol m <sup>-2</sup> )	$6.4\pm1.5\ 10^{-6}$	4.57±0.05 10-7	$9.84 \pm 1.10^{-6}$	$4.33 \pm 0.009 \ 10^{-7}$	$1.33 \pm 0.03 \ 10^{-6}$

Indeed, this catalyst exhibits the lowest oxygen chemisorption heat, see D<sub>2</sub> in Table 1, which indicates weaker bonding of atomic oxygen to the surface of the NaMnW/SiO<sub>2</sub> catalyst and, hence, lower contribution of the catalytic reaction network to the overall OCM reaction, since atomic oxygen is involved in a large number of catalytic steps (Alexiadis et al., 2014). This effectively slows down methane activation on NaMnW/SiO<sub>2</sub>, yet it also limits surface CO<sub>2</sub> formation. The surface production of carbon dioxide is further limited by the decreased oxidation rate of methyl radicals induced by their low sticking coefficient on the surface of the NaMnW/SiO<sub>2</sub> catalyst, see D<sub>11</sub>, Table 1. The methane hydrogen abstraction reaction enthalpy,  $(D_1, \text{ see Table 1})$  critically determines the higher activity of Sr/La<sub>2</sub>O<sub>3</sub> compared to that of LaSr/CaO under OCM reaction conditions. As can be seen in Table 1, Sr/La<sub>2</sub>O<sub>3</sub> exhibits a less endothermic Elev-Rideal methane H-atom abstraction step,  $D_1$ . The corresponding hydroxyl chemisorption heat on the Sr/La2O3 surface was calculated equal to 278 kJ/mol (Alexiadis et al., 2014), while for LaSr/CaO the same was limited to 257 KJ/mol. Differences in oxygen chemisorption heat  $(D_2)$  and active site density  $(D_{16})$ 

 $Sr/L_{a2}O_3$ . As can be readily seen in Table 1 and was also reported in previous work (Alexiadis et al., 2014), the higher activity of Sr/La<sub>2</sub>O<sub>3</sub> compared to that of SnLi/MgO is attributed to the higher values for D<sub>2</sub> and D<sub>16</sub> and the lower D1. Furthermore, the SnLi/MgO catalyst presents a higher selectivity to C2 products than LaSr/CaO due to the lower oxygen chemisorption heat (D<sub>2</sub>) and the lower value for methyl radical sticking coefficient on its surface  $(D_{11})$ . However, a comparison between LaSr/CaO and SnLi/MgO catalyst in terms of methane activation is not such a straightforward task. The latter catalyst exhibits lower methane H-atom abstraction reaction enthalpy, D<sub>1</sub>, yet the oxygen chemisorption heat, D<sub>2</sub>, and the density of active sites, D<sub>16</sub>, on its surface are limited compared to LaSr/CaO catalyst. Given the differences in operating conditions used in the determination of the OCM kinetics, an unequivocal comparison among the various catalysts is only feasible via microkinetic modelling. For this purpose, experimental points produced over Sr/La<sub>2</sub>O<sub>3</sub> were simulated by the model employing the descriptor

are less critical for explaining the higher activity of

values pertaining to Li/MgO and SnLi/MgO catalysts (Alexiadis et al., 2014), as well as the LaSr/CaO and NaMnW/SiO<sub>2</sub> catalysts, see Table 1. As shown in Figure 1, the methane conversion over Sr/La<sub>2</sub>O<sub>3</sub> catalyst is simulated approximately 2, 5 30 and 33 times higher than over the LaSr/CaO, SnLi/MgO, NaMnW/SiO<sub>2</sub> and Li/MgO catalysts, respectively, under identical operating conditions.

At a space time equal to 0.35 kg s mol<sup>-1</sup>, Sr/La<sub>2</sub>O<sub>3</sub> and Li/MgO exhibit a similar selectivity to C2 products of about 25%, with the former catalyst being much more active. A much higher C<sub>2</sub> selectivity, amounting to 80 % is simulated for the NaMnW/SiO2 catalyst, irrespective of the applied space time, under the investigated conditions. As mentioned before, this can be assigned to the low values for oxygen chemisorption heat and methyl radicals sticking coefficient obtained for these catalysts, see Table 1. SnLi/MgO seems to present lower selectivity than NaMnW catalyst toward C<sub>2</sub> products, followed by LaSr/CaO catalyst.



Figure 1. Conversion (full lines) and selectivity (dashed lines) vs. space time

The C<sub>2</sub> selectivity as a function of methane conversion is presented in Figure 2 so that a more concrete comparison can be made among the catalysts with respect to C<sub>2</sub> selectivity. As clearly seen under OCM operating conditions that lead to similar CH<sub>4</sub> conversion, i.e., around 1-2 %, by employing the microkinetic model, the five catalysts are ranked with respect to C2 selectivity as follows from high to low: Na-Mn-W/SiO<sub>2</sub> > Sn-Li/MgO> La-Sr/CaO > Sr/La<sub>2</sub>O<sub>3</sub> > Li/MgO.



Figure 2. Selectivity vs. conversion

#### Conclusions

The present OCM microkinetic model including catalyst descriptors enables the generic description of OCM reaction performances on 5 different catalysts belonging to 4 families based on a single reaction network. The applicability of the model was extended from alkali magnesia catalysts represented by Li/MgO and SnLi/MgO and alkaline earth lanthana catalysts represented by Sr/La<sub>2</sub>O<sub>3</sub> to two more catalyst familes, that is rare earth-promoted alkaline earth calcium oxide catalysts. represented by LaSr/CaO, and а NaMnW/SiO2 catalyst. The agreement between simulated and experimental conversions and selectivities on all five investigated catalysts for the complete range of experimental conditions was adequate.

The Sr/La<sub>2</sub>O<sub>3</sub> catalyst was found to be the most active while NaMnW/SiO<sub>2</sub> proved to be the most selective catalyst towards C<sub>2</sub> products. By employing the model, it was established that the catalyst descriptors which control the activity are: the reaction enthalpy of methane H-atom abstraction, the oxygen chemisorption enthalpy and the active site density. Likewise, C<sub>2</sub> selectivity is governed by two catalyst descriptors, that is the oxygen chemisorption enthalpy and the methyl radical sticking coefficient. Hence, a microkinetic model including catalyst descriptors can provide guidelines for the development of optimal catalytic systems.

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## COMBUSTION CHEMISTRY VIA METADYNAMICS: BENZYL DECOMPOSITION REVISITED

Daniela Polino and Michele Parrinello<sup>\*</sup> Department of Chemistry and Applied Biosciences, ETH Zurich and Facoltà di Informatica, Istituto di Scienze Computazionali, Università della Svizzera Italiana, Via G. Buffi 13, 6900 Lugano Switzerland

#### Abstract

Large polycyclic aromatic hydrocarbons (PAHs) are thought to be responsible for the formation of soot particles in combustion processes. However, there are still uncertainties on the course that leads small molecules to form PAHs. This is largely due to the high number of reactions and intermediates involved. Metadynamics combined with ab initio molecular dynamics can provide a very precious contribution because offers the possibility to explore new possible pathways and suggest new mechanisms. Here, we adopt this method to investigate the chemical evolution of the benzyl radical, whose role is very important in PAHs growth. This species has been intensely studied, and though most of its chemistry is known, there are still open questions regarding its decomposition. The simulation reproduces the most commonly accepted decomposition pathway and it suggests also a new one which can explain recent experimental data that are in contradiction with the old mechanism.

#### Keywords

Combustion, Benzyl, Metadynamics, ab initio.

#### Introduction

Soot formation has been extensively studied in the past years and nowadays is commonly accepted that soot particles are formed by the agglomeration of aromatic species, especially large polycyclic aromatic hydrocarbons (PAHs) (Frenklach 2002). However, there are still uncertainties on the molecular-growth processes leading small precursor molecules to form large PAHs. Among the species formed during combustion, resonance-stabilized free radicals (RSFRs) are believed to play a critical role in the mechanism of formation of the first aromatic ring and its subsequent growth (Hansen et al. 2012).

The reactions one encounters studying PAHs formation and growth are characterized by very complicated mechanisms. The strategy commonly adopted to investigate such reactions relies on (1) the formulation of a plausible mechanism identified by chemical intuition, (2) location of the transition states (TS) and (3) evaluation of the reaction rate using advanced techniques based on transition state theory (TST). In the last decades there has been much progress in the evaluation of accurate rate coefficients. Many efforts have been made to overcome TST limitations and new methodologies have been proposed to take into account tunneling effects for low temperature reactions, anharmonicity and recrossing, as reviewed in a recent paper of Klippenstein et al. (Klippenstein et al. 2013). The application of these advanced methods to complex combustion systems, such as those involving resonance-stabilized radicals, is based on educated guesses of the reaction mechanism.

Unfortunately, there are numerous reactive paths accessible to these species, even considering molecules that have only few atoms. This aspect can make the identification of the main reaction paths difficult.

Metadynamics combined with ab initio molecular dynamics can offer a useful contribution. Metadynamics is an enhanced sampling technique where the exploration of the configurational space is boosted by the addition of a time dependent repulsive bias potential that discourages the system from revisiting already sampled configurations. This potential acts on slow degrees of freedom, named collective variables (CVs), which give a coarse grain description of the phase space. There are two significant advantages in the use of metadynamics. First of all, very little knowledge of the possible reaction mechanisms is required. Second, at the end of the simulation an estimate of the free energy surface (FES) can be obtained from the bias potential deposited during the calculation. In this way both energetic and entropic contributions are accounted for without introducing any approximation or any particular treatment for the internal molecular motions. These capabilities can be especially appealing in combustion science and in particular for the study of soot formation.

Numerous theoretical studies have investigated the reactive properties of many resonance-stabilized radicals. Among these, the benzyl radical has been considered one of the principal actors of the growth mechanism of PAH, as it is produced in high concentration during the pyrolysis and combustion of fuel and is characterized by a high chemical stability given its resonant structure. A recent advance in the understanding of benzyl reactivity has come from the theoretical work of Derudi et al. (Derudi et al. 2011),

<sup>\*</sup>To whom all correspondence should be adressed

who proposed that benzyl has two main decomposition products: fulvenallene and benzyne (C<sub>6</sub>H<sub>4</sub>). Their reaction model was able to explain the experimental evidences of Sivarmakrishnan et al. (Sivaramakrishnan et al. 2011) that were not compatible with a model in which only fulvenallene was formed. A new experimental study conducted by Lemieux in his PhD work (Lemieux 2013) adds further support to the proposed mechanism, having detected CH<sub>3</sub> and C<sub>6</sub>H<sub>4</sub> species during benzyl pyrolysis. However, in spite of the significant improvement over the original model, still some aspects of the reaction mechanism remain unclear. In particular isotope substitution experiments performed both by Sivaramakrishnan et al. (2011) and more recently by Lemieux suggest that the hydrogen produced can come from the aromatic ring and also from the side chain. The latter feature cannot be explained by the model of Derudi et al. (2011) Thus, we decided to investigate again benzyl chemical reactivity adopting well tempered metadynamics (WT-MTD) combined with ab initio molecular dynamics, with the purpose of addressing the remaining open questions on its decomposition mechanism, and more in general demonstrate the potential that metadynamics can have in the study of combustion kinetics.

#### Results

In the next section are described the results obtained through WT-MTD simulation and also taking advantage of its multiple walkers extension. Here, we did not expect to converge the free energy explored, because given the large number of minima, the simulation would have taken too long to fully converge. Nonetheless, qualitative information can be gathered adopting the WT-MTD scheme as a tool for discovering new pathways and new isomers. To highlight this point, the WT-MTD results were converted into stationary points along the reaction pathways observed. In addition, the resulting potential energy surface was calculated with more accurate electronic structure methods and compared to the corresponding free energy surface in which entropies were computed adopting the harmonic oscillator approximation combined with the 1D hindered rotor approach.



Figure 1. PES of the main benzyl decomposition channels described in Derudi et al. with the addition of a third decomposition reaction (TS7) identified in this work. Energies (kcal mol-1) were calculated at the

#### CCSD(T)/CBS(cc-pVDZ/cc-pVTZ) level. ZPE corrections computed at the B3LYP/6-31+G(d,p) level are included. WT-MTD Simulations

A first explorative WT-MTD run was performed at 1500 K adopting as CVs the number of rings and the angle spans the tertiary carbon atom of benzyl and the two adjacent carbons that belong to the aromatic ring. Simulations were carried out with a bias factor of 30, and a fast depositing rate, 25 fs. The initial hills height was 7 kcal/mol and the width of the hills equal to a fraction of the oscillations of the CVs monitored during a short MD simulation (0.1 for the number of rings and 0.02 for the angle). The system was first equilibrated at the assigned temperature with a MD simulation of 10 ps. In a second moment, we performed a multiple walkers WT-MTD simulation at 1500 K with 5 walkers whose bias potential was updated every 0.8 ps. Each walker deposited a Gaussian hill every 0.4 ps with an initial height of 7 kcal/mol and a bias factor equal to 8. The starting configurations chosen were the first five minima found in the previously described metadynamics simulation.

The first relevant outcome of the present study has been the reproduction of one of the main decomposition channels proposed for benzyl. The path connecting benzyl to the 4-vinylidene-cyclopentenyl radical observed in the first explorative simulation, in fact, followed the same reaction mechanism that Cavallotti et al. (2009) identified as one of the favored decomposition paths that leads to the formation of fulvenallene, as illustrated in scheme 1.



Scheme 1. Benzyl decomposition mechanism proposed by Cavallotti et al.(2009)

This result adds further support to this mechanism as one of the main decomposition channel of benzyl, which had been lately called into question by the isotope experiments of Sivaramakrishnan et al. (2011) and Lemieux (2013). In fact, considering only this mechanism one cannot explain how the H atom lost by benzyl can originate both from the side chain and the ring portion. This discrepancy, though, will be clarified below with the description of the second result obtained in the present study.

In Fig. 1 we show the most accepted mechanism for benzyl decomposition, as it was described in Derudi et al. (2011), with a third new decomposition channel which has been found during the multiple walkers MTD simulation. The new path foresees the simple loss of a hydrogen atom (TS7) from the side chain of 4-vinylidene-cyclopentenyl, intermediate 4. In the past intermediate 4 had been considered only as a precursor to fulvenallene. Here instead, we observed that a hydrogen atom can also be lost from the CH<sub>2</sub> group of the side chain, forming the stable 2-

ethynylcyclopentadiene, whose electronic energy is only 1.6 kcal/mol over that of fulvenallene.

Sivaramakrishnan et al. (2011) suggested that the H atom lost from the side chain comes from the Hdissociation of the cycloheptatetraenyl radical. This reaction however has a very large energy barrier (101.7 kcal/mol) and it cannot justify the large amount of H atoms detected. In contrast, the reaction that forms 2ethynylcyclopentadiene is in competition with the production of fulvenallene and it should be able to explain the experimental results. To support this suggestion we computed the branching ratios for the two H-loss channels estimated as the ratio between the single rate coefficients and the total rate of benzyl H removal given by their sum. Rate coefficients were calculated applying standard transition state theory and assuming benzyl as the reactant and TS4 and TS7 as the rate limiting steps. Scanning the potential energy surface of the side-chain H loss reaction along the length of the C-H breaking bond, it was determined that this dissociation does not proceed through a saddle point. Thus to estimate the corresponding rate coefficient it was applied the variational form of the transition state theory. The results are depicted in Fig. 2 and compared with the fitted experimental data of Sivaramakrishnan et al. (2011) obtained analyzing the thermal decomposition of C<sub>6</sub>H<sub>5</sub>CD<sub>2</sub> with H and D atom ARAS detection. In their study, the rate of formation of H corresponds to the H lost from the ring (here denoted as H1 loss), while the rate of formation of D atoms corresponds to the H loss from the side chain (H2 loss). The good agreement between our results and the experiment suggests that the new H loss channel proposed is most likely responsible for the production of the D atoms detected during C<sub>6</sub>H<sub>5</sub>CD<sub>2</sub> thermal decomposition. This is however only a preliminary result and a more detailed kinetic analysis needs to be performed.

Another interesting secondary result obtained from our WT-MTD simulations has been the identification of a new path leading to acetylene and a C<sub>5</sub>H<sub>5</sub> species. For a long time, it has been assumed that benzyl could decompose directly to acetylene and cyclopentadienyl (cC<sub>5</sub>H<sub>5</sub>). For this reason, several reactive channels that could lead benzyl to decompose into  $cC_5H_5$  radical and acetylene have been proposed. (Jones et al. 1997; Fascella et al. 2005; Cavallotti et al. 2009) Among these, the one passing through the conversion of benzyl into the cycloheptatetraenyl radical (cC<sub>7</sub>H<sub>7</sub>) and its successive fast decomposition into cC5H5 radical and acetylene has been classified as the less activated. (Fascella et al. 2005; Cavallotti et al. 2009) This path, though, has never been considered as one of the main decomposition mechanisms, because the reaction rate calculated at 1500 K (10 s<sup>-1</sup>) was lower than that experimentally determined (Oehlschlaeger et al. 2006) at the same temperature for benzyl overall decomposition (1500 s<sup>-1</sup>).

Metadynamics during the first explorative run was capable to find a new path to acetylene and  $C_5H_5$ .



Figure 2. Branching ratios fitted from experimental data of Sivaramakrishnan et al.(2011) Black diamonds for H1 loss (standard deviation is  $\pm 0.07$ ), black crosses for H2 loss (standard deviation is  $\pm 0.03$ ). Lines represent branching ratios calculated considering the TST rate constants of TS4 (H1 loss – red solid line) and TS7 (H2 loss – blue solid line). Dotted lines show the confidence limit of the calculated branching ratios corresponding to a deviation of a factor of 2 in the rate coefficients.

Notably, the C5H5 species formed in our MTD simulation is not cyclopentadienyl as assumed in most benzyl decomposition mechanisms, but the 2-ethynylpropenyl radical. In Fig. 3 are shown the energies of the structures discovered, compared to the corresponding free energies. It is possible to see how the entropic contribution substantially alters the landscape and those reactions that appeared to be too slow, because of the high electronic energies, become more accessible thanks to the entropic effects. We thus explored the possibility that this new path might play a role in benzyl decomposition comparing the reaction rate relative to the rate limiting step of the new mechanism (TS10) with the rate of the old path as it was calculated by Cavallotti et al. (2009) but with the activation energy calculated here with a higher quantum mechanical method. At 1500 K the largest energy barrier that benzyl has to overcome to convert into 2ethynyl-propenyl and C<sub>2</sub>H<sub>2</sub> is 98.6 kcal/mol, whereas, the energy barrier that benzyl has to overcome to interconvert into cC7H7 is about 85.6 kcal/mol.



Figure 3. Electronic (upper black) and free (lower red) energies of the discovered  $C_5H_5 + C_2H_2$  path. Energies (kcal mol-1) were calculated at the CCSD(T)/CBS(ccpVDZ/cc-pVTZ) level. ZPE corrections computed at the B3LYP/6-31+G(d,p) level are included. Entropies were calculated adopting the HR-HO approach at 1500 K.



Figure 4. Electronic (upper black) and free (lower red) energies of the path leading to the stable dimethylenecyclopentenyl structures discovered. Energies (kcal mol<sup>-1</sup>) were calculated at the CCSD(T)/CBS(ccpVDZ/cc-pVTZ) level. ZPE corrections computed at the B3LYP/6-31+G(d,p) level are included. Entropies were calculated adopting the HR-HO approach at 1500 K.

However, to these energy barriers are associated comparable reaction rates which are respectively, 7.3 s<sup>-1</sup> for the new mechanism and 3.8 s<sup>-1</sup> for the old one. The sum of the two accounts as ~ 1% of the total rate of decomposition (823 s<sup>-1</sup>) calculated by Sivaramakrishnan et al. (2011) fitting the experimental data. Thus, we can assume that the newfound path together with the one proposed by Cavallotti et al. (Fascella et al. 2005; Cavallotti et al. 2009) are the most favored reaction channels responsible for the formation of C<sub>5</sub>H<sub>5</sub> and acetylene. Nevertheless, both reactive channels offer only a minor contribution to the total benzyl decomposition rate.

Finally, a last unexpected result was the formation of two very stable C<sub>7</sub>H<sub>7</sub> isomers, the two dimethylene-cyclopentenyl structures, 11 and 14. We have calculated the energies and corresponding free energies of all the intermediates and transition states that are involved in the mechanism that leads to their formation, which are illustrated in Fig. 4. Analyzing this picture we can observe that the C<sub>7</sub>H<sub>7</sub> molecule has to pass through several concerted reactions to form the two dimethylene-cyclopentenyl structures. Consequently the energies of the transition states located on the PES are far higher than those described until now and so also the corresponding free energies. In contrast, the two dimethylene-cyclopentenyl radicals are very low in energy, only 16.6 and 17.5 kcal/mol higher in energy compared to benzyl. It would be thus rather interesting analyze if and how this chemical species can originate and chemically evolve in a combustion environment. Given their stability and particular form, in fact, they could play a significant role in larger PAH formation. For example, one may presume that 1,5-dimethylenecyclopentenyl could react with acetylene forming 4Hindene through a Diels-Alder reaction mechanism followed by an H atom loss.

#### Conclusions

In conclusion, the analysis of the FES explored thus far allowed us to gather some interesting

observations. First we have reproduced the mechanism proposed by Cavallotti et al. (2009) without taking advantage of a priori knowledge of the system. Secondly, we have proposed a new H-loss reactive channel that can answer the yet unexplained isotope experimental results of Sivaramakrishnan et al. (2011) and Lemieux. (2013) Moreover, we have identified a new path through which benzyl can decompose directly to acetylene and C5H5. This path, compared to the competing channel that leads to the formation of cyclopentadienyl and acetylene, presents a higher energy barrier but thanks to the entropic effect their reaction rates are actually comparable. Thus the newly found path with the old one can be considered so far the most probable routes to the direct formation of acetylene and a C<sub>5</sub>H<sub>5</sub> species. Finally, we have also discovered two new very stable isomers of benzyl that may become important actors in PAH growth.

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### A THEORETICAL AND EXPERIMENTAL INVESTIGATION OF THE REACTION OF O(<sup>3</sup>P) WITH PROPENE AND PROPYNE

I. Gimondi and C. Cavallotti\* Politecnico di Milano - 20131 Milano, Italy F. Leonori, N. Balucani, G. Vanuzzo and P. Casavecchia Università degli Studi di Perugia - 06123 Perugia, Italy

#### Abstract

In the present work, we report on a joint experimental and theoretical study aimed at determining channels and rates for the reaction of  $O(^{3}P)$  with propene and propyne. Theoretically, the triplet and singlet potential energy surfaces were investigated at the CASPT2 and CCSD(T) levels, with extension to the complete basis set limit. The system kinetics was investigated integrating the 1D master equation, accounting explicitly for the possibility of intersystem crossing (ISC) between the triplet and singlet potential energy surfaces. The computational predictions were compared with branching ratios derived from crossed-molecular-beams experiments with mass-spectrometric detection at 9.3 kcal/mol collision energy ( $E_c$ ). It was found that the extent of intersystem crossing is controlled by the competition between the decomposition of the adduct formed by  $O(^{3}P)$  addition to propene or propyne on the triplet PES and the rate of ISC, so that ISC is more significant in propyne than in propene though the spin-orbit coupling at the minimum energy crossing point is smaller. Quite interestingly, for propene we found that at high  $E_cs$  and temperatures higher than 1000 K main products are formaldehyde and triplet ethylidene formed in a reaction channel that has never been identified or considered significant in previous kinetics studies at 300 K and that, as such, is not included in combustion kinetics models.

#### Keywords

O(<sup>3</sup>P), RRKM/Master Equation, Combustion; CASPT2; Crossed Beams Technique.

#### Introduction

The reactions of  $O(^{3}P)$  with propene and propyne are of considerable interest in combustion science since they represent the simplest examples of the reactivity of  $O({}^{3}P)$  with substituted alkenes and alkynes. As the reactivity of  $O(^{3}P)$  with ethene and ethyne has already been the subject of several investigations and is thus mostly established, the study of the title reactions is necessary in order to devise scaling rules to determine reaction rates of O(<sup>3</sup>P) with more complex alkenes ad alkynes. The reactions of O(<sup>3</sup>P) with propylene and propyne have been investigated both experimentally and theoretically (see Leonori et al., 2015, Savee et al., 2012, and references therein). While some aspects are well established for both reactions, such as the total reaction rate between 300 and 1500 K and the fact that intersystem crossing is relevant, much less is known about the nature of the products of the reaction and, most importantly, about the branching ratios among the most relevant reaction channels. In the present paper, we report some of the results of our recent investigation of the reactivity of O(<sup>3</sup>P) with propene and propyne. Due to the limited available space, we will mainly focus on the computational part of this study, and in particular on

the description of the portions of the triplet potential energy surfaces (PESs) that contribute mostly to the system reactivity, on the rate of the entrance channels, and on the extent of intersystem crossing.

#### Method

The computational and experimental tools used in the present study are described in detail in our recent publications and will therefore be only briefly summarized. On the experimental side, two supersonic beams of the reactants are crossed at 90° under singlecollision conditions in a large scattering chamber kept at about  $2 \times 10^{-6}$  mbar under operating conditions. The angular and velocity distributions of the reaction products are recorded by a triply differentially pumped, ultra-high-vacuum (UHV) (10<sup>-11</sup> mbar) detector equipped with a tunable electron impact ionizer followed by a quadrupole mass filter and an off-axis electron multiplier. The velocity of reactants and products is derived using single-shot and pseudorandom, respectively, TOF analysis (Casavecchia et al., 2009).

Theoretically, the  $C_3H_6O$  and  $C_3H_4O$  PESs were investigated at the CASPT2 level using the augcc-pVTZ basis set and a minimal active space to optimize the geometry and calculate vibrational frequencies. Energies were computed at the CCSD(T)

<sup>\*</sup> To whom all correspondence should be addressed

level using aug-cc-pVDZ and aug-cc-pVTZ basis sets and extrapolated to the complete basis set limit (Cavallotti et al 2014). In all the cases in which T1 diagnostics were greater than 0.02, energies were also computed at the CASPT2 level using the aug-cc-pVTZ basis set, increasing systematically the active space until convergence. Branching ratios were determined solving the 1D master equation over the calculated ab initio triplet and singlet PESs, accounting explicitly for inter system crossing (ISC) (Polino and Cavallotti, 2010, 2011). ISC rates were computed using Landau-Zener theory, while rate constants were computed in the rigid rotor harmonic oscillator approximation. The contribution of low frequency torsional vibrations to the density of states of PES stationary points was computed using a 1D hindered rotor model.

#### **Results and Discussion**

The triplet portions of the calculated C<sub>3</sub>H<sub>6</sub>O and C<sub>3</sub>H<sub>4</sub>O PESs used in the master equation simulations are shown in Figure 1. The reported reaction pathways do not represent all the possible reaction routes that were investigated, but only those that were found to contribute significantly to the system reactivity. In the following the analysis of the two reaction mechanisms is performed comparing similarities and discrepancies between pathways and energy barriers. Both the C<sub>3</sub>H<sub>6</sub>O and C<sub>3</sub>H<sub>4</sub>O PESs can be accessed through the addition of O either to the central or to the terminal C of the double (triple) bond of propene (propyne). In both cases addition to the terminal C is faster than addition to the central C, with a ratio between the rate of the two channels of about 3/1 for propene and 4/1 for propyne at 300 K, which decreases increasing the temperature. The difference in the reaction rates for the two channels is in part due to pre-exponential factors and in part to a slightly larger energy barrier for addition to the central C, which is about 0.3 kcal/mol higher than that for addition to the terminal C. There is however a large difference between the energy barriers for O(<sup>3</sup>P) addition to propene (0.16 kcal/mol) and propyne (1.9) kcal/mol, which slows down considerably the propyne reactivity with respect to that of propene. The total rates of the reactions of  $O({}^{3}P)$  with propene and propyne are reported in Figure 2, where they are compared with experimental data. In the case of  $O({}^{3}P)$ +propene, the total rate includes also the rate of the reaction of extraction of H, which is known to proceed at a rate that is comparable to that of addition as the temperature increases (Cavallotti et al., 2014). As it can be observed, calculated and experimental data are in good agreement. This supports the reliability of the adopted computational protocol, which uses CASPT2 energies calculated with the aug-cc-pVTZ basis set, (10e,9o) and (12e,11o) active spaces averaged over 2 states for propene and propyne, respectively, and the description of the methyl rotation at the saddle point using a hindered rotor model. The computational protocol is

similar to that used by Sabbah et al. (2007) to study the addition of propene to  $O(^{3}P)$ .

Following O addition to the terminal C, several reaction pathways become possible: H loss, H migration along the C chain, cleavage of the CH<sub>3</sub>CH-CH<sub>2</sub>O bond (only C<sub>3</sub>H<sub>6</sub>O PES), and intersystem crossing to the singlet PES. The O addition reaction is exothermic by 23.7 kcal/mol for propene and 51.8 kcal/mol for propyne. The well that is accessed on the  $C_3H_4O\ PES$  following O addition can exist in two rotational isomers,  $W_{cis}^{B}$  and  $W_{trans}^{B}$ , which differ for the relative orientation of O and the methyl group and can be interconverted through a rotation of the terminal CHO group via  $TS4^{B}$ . Since the energy barrier for this reaction is considerably low, the two isomers can be considered to be at equilibrium. However, since the reaction pathways that they can access are different. they were considered as separate species in the master equation simulations. The same applies to all the wells that can be accessed from  $W1^{B}$ . Minimum energy crossing points (MECP) between the triplet and the singlet PES were searched on the triplet PES as described in Cavallotti et al. (2014). In both cases two intramolecular geometric parameters had to be modified simultaneously while relaxing all the others degrees of freedom in order to find the MECP. It was found that the minimum energy S1/S0 crossing point lies about 1 kcal/mol and 12 kcal/mol above the energy of the entrance wells for propene and propyne, respectively. Energy barriers for H loss and H migration on the C<sub>3</sub>H<sub>4</sub>O PES are considerably higher than those found on the C<sub>3</sub>H<sub>6</sub>O PES for similar reaction pathways, which favors ISC on the C<sub>3</sub>H<sub>4</sub>O PES. However, on the other side, the spin orbit coupling coefficient calculated at the MECP is higher on the  $C_{3}H_{6}O$  PES (about 35 cm<sup>-1</sup>) than on the  $C_{3}H_{4}O$  PES (about 24 cm<sup>-1</sup>). One of the fastest reaction pathways, which is competitive with ISC on both PESs, is H loss from the terminal C, which leads to the formation of CH<sub>3</sub>CHCHO+H on the C<sub>3</sub>H<sub>6</sub>O PES and to CH<sub>3</sub>CCO+H on the C<sub>3</sub>H<sub>4</sub>O PES. CH<sub>3</sub>CCO+H can be formed on the C<sub>3</sub>H<sub>4</sub>O PES through two distinct transition states, with one of the two,  $T\mathfrak{S}_{t}^{B}$ , considerably faster than the other. While H transfer was found to contribute negligibly to the system reactivity on the C<sub>3</sub>H<sub>6</sub>O PES, it was found that this was not the case for the C<sub>3</sub>H<sub>4</sub>O PES. Thus, the  $W1^B$  well can be interconverted to <sup>3</sup>CH<sub>2</sub>CHCHO (W2<sup>B</sup>) <sup>3</sup>CH<sub>3</sub>CHCO, and <sup>3</sup>CH<sub>2</sub>CCHOH. Conversion to <sup>3</sup>CH<sub>3</sub>CHCO and <sup>3</sup>CH<sub>2</sub>CCHOH is followed by rapid decomposition to <sup>3</sup>CH<sub>3</sub>CH+CO and CH<sub>2</sub>CCH+OH, so that only the final products of these reactions pathways are shown in Figure 1. W2<sup>B</sup> has a more complex reactivity, as it can decompose to  $C_2H_3\text{+}HCO$  or  $^3C_2H_4$  +CO, with the latter channel being dominant over the other. Differently from what found on the C<sub>3</sub>H<sub>4</sub>O PES, the cleavage of the CH<sub>3</sub>CH-CH<sub>2</sub>O bond for W1<sup>A</sup> on the C<sub>3</sub>H<sub>6</sub>O PES is an important reaction channel.



Figure 1. Triplet PES for the reactions of  $O({}^{3}P)$  with  $C_{3}H_{6}$  (top, A) and  $C_{3}H_{4}$  (bottom, B) used in the master equation simulations. The reported PESs contain only the reactions that were found to contribute significantly to the system reactivity. Energies are reported in kcal/mol relatively to the reactants. The t and c subscripts in the  $C_{3}H_{4}O$  PES refer to transition states connected to wells with cis or trans structures (named depending on the relative positions of O and  $CH_{3}$ ). Dotted lines mean the reaction is not elementary but involves the formation of at least one intermediate well.

The reactivity that follows addition to the central C on the triplet PES is much simpler than that found for addition to the terminal C, as the main reaction channels are only two: methyl loss and ISC, with the first being in general faster than the second.

Two different sets of master equation simulations were performed for each of the two investigated systems. In the first case we simulated the CMB experiments, thus adding the energy of the colliding beams to the exothermicity of the entrance well, while in the second we simulated a 300K thermal environment. The CMB simulations revealed that ISC increases considerably going from propylene, where it is about 20%, to propyne, where it accounts for about 45% of the system reactivity. The ISC branching ratio is higher in the 300K thermal simulations, which predict an ISC of 60% for propylene and 80% for propyne. The increase of the extent of ISC in the thermal with respect to the CMB simulations is determined by the increase of the rates of the reactions channels that are competitive with ISC, which is caused by the redistribution of the energy of the colliding beams in the internal degrees of freedom of the entrance wells. The increase in the ISC branching ratio found for propyne with respect to propylene is determined by the fact that the reaction channels that are alternative to ISC require overcoming energy barriers that are considerably larger than those found for propylene, which gives a significant competitive advantage to ISC over the other reaction channels. The calculated ISC rates are in good agreement with those extrapolated from the experimental measurements.



Figure 2. Total rates of the reactions between  $O({}^{3}P)$ and propene (calculated: continuous line; experimental full symbols) and propyne (calculated: dotted line; experimental empty symbols)

#### Conclusions

The present simulations show that intersystem crossing is in an important reaction channel for the reaction of  $O(^{3}P)$  both with propyne and propene. Its extent is controlled by the competition between the decomposition of the adduct formed by  $O(^{3}P)$  upon addition to the reactant and the rate of ISC, so that ISC is more significant in propyne than in propene though the spin-orbit coupling at the minimum energy crossing point is smaller.

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# An analysis of the role of the C=C double bond on the fate of alkenylperoxy radicals

Yawei Chi,<sup>a, b</sup> Chung K. Law,<sup>a, c</sup> Xiaoqing You<sup>a, b\*</sup>

<sup>a</sup> Center for Combustion Energy, Tsinghua University, Beijing 100084, China

<sup>b</sup> Key Laboratory for Thermal Science and Power Engineering of Ministry of Education, Tsinghua University, Beijing

100084, China

<sup>c</sup> Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544, USA

#### Abstract

The major components of biodiesel fuels usually consist of one or more C=C double bonds in their molecular structure, which are known to influence strongly their low-temperature combustion characteristics. While alkylperoxy radicals (RO2), the key intermediates in the low-temperature oxidation of alkanes, have been widely investigated, the role of the peroxy radicals with C=C double bond(s) is less understood. In this study, 2-heptene and 2,5-heptadiene are selected to represent the long-chain biodiesel molecules having one and two C=C double bond(s), respectively. The fate of the various peroxy radicals of these two molecules is investigated by using quantum chemistry methods at the CBS-QB3//B3LYP-6-311G(d,p) level and canonical/variational transition state theories. Results show that at low temperatures (500-900 K), the peroxy radicals of 2,5-heptadiene that has four vinylic and three allylic carbon atoms can be neglected; while for 2-heptene, the 2-heptenylperoxy radicals with O<sub>2</sub> bonded with the alkylic carbons favor H-atom shift reactions, with their rates mostly influenced by the size of the cyclic transition state.

#### Keywords

Biodiesel, C=C double bond, alkenylperoxy, H-atom shift, decomposition.

#### Introduction

Recently, there have been increased interests in the study of biodiesels as supplements or replacements for conventional petroleum-based fuels (Demirbas, 2007;Graboski and McCormick, 1998).<sup>1,2</sup> The major components of biodiesel fuels contain a large fraction of C=C double bonds, which are known to have a strong influence on the low temperature combustion of biodiesel fuels (Westbrook et al., 2011; Westbrook et al., 2013).<sup>3,4</sup> However, investigations of alkenyl peroxy radicals have been carried out only in recent years. Specifically, the thermochemic properties and kinetics of the allyl radical (CH2=CHCH2 $\cdot$ ) + O<sub>2</sub> reaction system were studied by Lee et al. with quantum chemistry and RRKM/master equation simulations (Lee and Bozzelli, 2005);<sup>5</sup> the unimolecular reactions of the 3-butenyl (•CH2CH2CH=CH2) radicals as well as the subsequent unimolecular reactions of the 3butenylperoxy radicals were investigated by Miyoshi (Miyoshi, 2010);<sup>6</sup> while Zhang et al. investigated the reactions of RO2, QOOH, and O2QOOH of alkanes and alkenes by the CBS-QB3 method (Zhang and Dibble, 2011).7

Few studies have been focused on whether the dissociation of RO2 is competitive with the intramolecular H-shift reactions of RO2 of alkenes under the influence of the C=C double bond, which changes the C-H and C-O2 bond dissociation energy. In this study, we address this question by using

chemical calculations quantum and canonical/variational transition theories state (Klippenstein and Harding, 1999)<sup>8</sup> to explore the effects of the C=C double bond on the unimolecular reactions of alkenyl peroxy radicals, including intramolecular H-migration and dissociation reactions. 2-Heptene and 2,5-heptadiene are chosen to represent long-chain alkenes that have a number of different types of reaction sites. All of the cis-trans isomers are included because the trans-conformers are more stable while the cis-conformers are more common in natural fatty acids (Zhang and Dibble, 2011; Dibble et al., 2012).7,9

#### Methods

All of the structure optimization was conducted by using B3LYP/6-311G(d,p) with the Gaussian 09 package of programs<sup>10</sup>. The high-level composite method CBS-QB3 was used for accurate energy calculations. The high pressure limit (HPL) rate constants of reactions with apparent transition states were calculated by canonical transition state theory (CTST), as implemented in the program package Multiwell<sup>11,12</sup>. One-dimensional tunneling corrections based on asymmetric Eckart potentials were included in calculating the rate contants. The variational transition-state theory (VTST) was used for barrierless reaction rate constant calculations.

Corresponding author: xiaoqing.you@tsinghua.edu.cn 119

For simplicity, the names of species and reactions are all shown in abbreviated form. We used 'C' and 'T' to represent cis- and trans- conformers, respectively. 'P' is peroxy, 'R' radical, 'S' H-shift reactions and 'D' dissociation of the RO2 adduct to  $R + O_2$ . Thus, CnP and CTnP represent n-peroxy-2(cis)-heptenyl and nperoxy-2(cis),5(trans)-heptadienyl with  $O_2$  bonded on the *n*th carbon, respectively. For CnPmR and CTnPmR, n refers to the peroxy radical site and m refers to the hydrogen abstraction site. Then an addition of 'S' to CnPmR refers to the H-shift reaction from CnP to CnPmR (H shift from *m*th carbon to peroxy that bonded on *n*th carbon) via a cyclic transition state. CnPD represents the dissociation of the CnP adduct to CnR +  $O_2$ .

#### **Results and discussion**

#### Bond Dissociation Energy (BDE)

The BDEs of C-H and C-O2 in 2(cis)-heptene and 2(cis),5(trans)-heptadiene are displayed in Figure 1. For 2-heptene, the C(villylic)-H (hereafter called C<sub>v</sub>-H) bond is the strongest, followed by the C(primary)-H  $(C_p-H)$  BDE, which is slightly higher than that of the secondary. The BDE of C(allylic-secondary)-H (Cas-H) is the smallest. Because there are two double bonds in 2,5-heptadiene, the C(double-allylic)-H (Cda-H) BDE is even smaller. The rule of BDE of C-O2 is slightly different from that of the C-H bond, in which the primary C-O2 bond is weaker than the secondary C-O2 bond. The double-allylic C-O2 BDE is still the smallest. As the vinylic C-H bonds have been proven to be too strong to rupture at low temperatures in previous studies, reactions of the vinylic peroxy radicals can be excluded.





Figure 1. C-H BDE of (a) cis-2-heptene and (b) 2(cis),5(trans)-heptadiene, C-O2 BDE of (c) cis-2heptene and (d) 2(cis),5(trans)-heptadiene, calculated at CBS-QB3 level

# Comparison of the dissociation and intramolecular hydrogen-shift reactions of RO2

It is seen from the BDE analysis that the  $C_{as}$ -O2 bond is far weaker than the typical  $C_{s}$ -O2 bond, while the  $C_{da}$ -O2 bond is even weaker. If the dissociation of RO2 is faster than what is expected, then the isomerization of RO2 would be less important. To explore the effect of the C=C double bond on the intramolecular H-transfer and dissociation reactions, alkenylperoxy radicals of 2,5-heptadiene and 2-heptene with O<sub>2</sub> bonded on every carbon were chosen to be compared. Figure 2 shows the potential energy surfaces for the two unimolecular reactions for several representative peroxy radicals.



Figure 2. Potential energy diagrams for H-shift and dissociation reactions of (a) n-peroxy-2-heptene (n=4,5), and (b) n-peroxy-2(cis),5(trans)-heptadiene (n=1,4)

For the dissociation reactions, the well of C5P is much deeper than C4P (by 16 -18 kcal/mol) due to the higher C-O2 BDE of the H abstraction site. The well of CT4P is much shallower than CT1P (about 6 kcal/mol) for the dissociation reactions due to the lowest Cda-O2 BDE. The barrier heights of the H shift reactions for C4P are roughly the same as the entrance C4R+O2, which implies that the C4P can either go through H-shift dissociation or reactions with an equivalent level of difficulty. All of the H-shift reactions of C5P need less energy than its dissociation reactions. This may suggest that the hydrogen transfer reaction C5P1RS via an eight-membered ring transition state thermodynamically favored than is the dissociation reaction for C5PD. The barrier of the Hshift reaction of CT1P is 6.5 kcal/mol lower than that of its dissociation reaction.

A comparison of the computed high-pressurelimit rate constants of the dissociation reactions and Hshift reactions of n-peroxy-2(cis),5(trans)-heptadiene (n=1,4) and n-peroxy-2-heptene (n=1,4,5) is shown in Figure 3a and 3b respectively.



Figure 3. High-pressure-limit rate constants of the Hshift reactions and dissociation reactions for (a) nperoxy-2(cis),5(trans)-heptadiene (n=1,4) and (b) nperoxy-2-heptene(n=1,4,5)

The rate constant of the dissociation reaction CT4PD is the highest among all reactions shown in Figure 3a, which implies that the dissociation reaction CT4PD is dominant for CT4P. At 500-900 K, the

dissociation reaction CT1PD and the H-shift reaction CT1P4RS through a 7-membered-ring transition state are competitive. In Figure 3b, the dissociation rate constant for the allylic-primary alkenyl peroxy radical C1P is indistinguishable from that for allylic-secondary alkenyl peroxy radical C4P, and they are much higher than that of the secondary radical C5P. For all species in Figure 3b, the dissociation reaction is not competitive with that of H-transfer, except in the case of C5P, which is stable at low temperatures with respect to dissociation to C5R+O<sub>2</sub>. In summary, the favorable path is the intramolecular H-transfer reaction occurring on allylic-primary alkenylperoxy radical of 2(cis),5(cis or trans)-heptadiene (CC1P, CT1P) and secondary or primary alkenyl peroxy radical of 2heptene(C5P, C6P, C7P, T5P, T6P, T7P).

# The rate rules of intramolecular hydrogen transfer reactions

The H-shift reactions of n-peroxy-2-heptene (n=5,6,7) were calculated and compared. Three structural features that impact most of the rate constants are discussed below.

#### (1) Effect of the hydrogen-abstraction sites

The H-shift reaction rate constants via sixmembered-ring and five-membered-ring transition states are shown in Figure 4a, respectively. They vary substantially with various hydrogen-abstraction sites. The influence of the hydrogen-abstraction sites on the H-shift reaction rates follows the order: allylic secondary > secondary > primary > vinylic site. The hydrogen shift reactions of H shifted from the vinylic carbon can be estimated to be unimportant since the rate constants for this type of reactions are two orders of magnitude lower than that of the allylic-secondary carbon. For H-shift reactions with the transition state with the same ring size, the entropy decreases do not change significantly with various hydrogen-abstraction sites.

#### (2) Effect of the ring size

The high-pressure-limit rate constants for the Hshift reactions of RO2 radicals via cyclic transition states of various sizes are compared in Figure 4b (H shift from the allylic-secondary carbon). The activation energies that reflect the ring-strain energy of the transition states do not change much when the ring size increases from 6 to 8 (1~2 kcal/mol) members and increase significantly for the ring size of 5 (8~10 kcal/mol). When the ring size is increased from 5 to 6 members, H-shift rate the constants are correspondingly increased by 2~4 orders of magnitude.

Compared with the effect of the ring size, the effect of hydrogen-abstraction site seems to be less important.

(3) Effect of the C=C double bond in the cyclic transition state

Figure 4c shows the H-shift reaction rate constants via the cyclic transition state with or without a C=C double bond. For the eight-membered ring transition state, it seems that whether the C=C double bond is contained by the cycle has no effect on the rate constants, while a slight reduction of rate constants are found in the seven-membered ring H-shift reactions due to the C=C double bond in the cycle.



Figure 4. Calculated rate constants of the H-shift reactions at the high-pressure limit

#### Conclusions

The influences of the C=C bond on the fate of alkenylperoxy can be summarized as follows: (1) Reactions of alkenylperoxy with  $O_2$  bonded on the vinylic carbon can be neglected. (2) For all n-peroxy-2,5-heptadiene(n=1,4), the H-shift reactions can be

ignored except for CT1P4RS or CC1P4RS which are competitive with the dissociation reactions. (3) For 2heptene, the H-shift reactions of n-peroxy-2-heptene (n=5,6,7) are favored at low temperatures. The rate rules of the H-shift in RO2 of 2-heptadiene reveal the main influence factors in order of importance: the size of cyclic transition states, hydrogen abstraction site and whether C=C double bond is in the ring. Under the same condition, the rates of six-membered-ring transition state are faster than seven-membered and five-membered ones. The influence of H abstraction sites on H-shift reaction rates follows the order: allylic secondary > secondary > primary > vinylic site. C=C double bonds in the ring of transition states decrease the H-shift rate, but the effect is weaker than the other two factors

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## A SYSTEMATIC STUDY OF RADICAL ADDITION REACTIONS TO SUBSTITUTED BENZENES AND THE REVERSE BETA-SCISSION REACTIONS

Hans-Heinrich Carstensen<sup>\*</sup>, Kevin M. Van Geem, Marie-Francoise Reyniers and Guy B. Marin Laboratory for Chemical Technology, Ghent University Technologiepark 914, 9052 Ghent Belgium

#### Abstract

The addition reactions of H atoms and carbon- and oxygen-centered radicals to substituted benzene as well as the reverse  $\beta$ -reactions have been studied with the CBS-QB3 electronic structure method. As expected, the nature of the adding or leaving radical strongly influences the reactivity. The  $\beta$ -scission reactions are significantly faster if highly substituted radials are formed, while the elimination reactions of H atoms or methyl radicals are particularly slow. Substituents to the ipso carbon alter the rate coefficients for the addition reactions only to a minor degree. The same was found for substituents in ortho, meta or para position to the addition site. This means that group additivity can easily be applied to calculate rate coefficients for these reactions, because as a first approximation only one major contribution, which describes the reactivity difference between the adding radical compared to that used in the reference reaction, needs to be accounted for.

#### Keywords

Radical addition reactions, beta-scission reactions, CBS-QB3, aromatics.

#### Introduction

Aromatic molecules play an important role in almost all pyrolytic reaction systems. They often act as precursors for deposit (e. g. in solid oxide fuel cells or steam crackers) or soot (flames) formation. Large amounts of substituted benzenes are generated in the fast pyrolysis of ligno-cellulosic biomass and considerable effort is devoted to use this process as a source for high-value organic chemicals. To find optimal pyrolysis conditions, a good understanding of the elementary step reactions is necessary. This generally means that detailed kinetic models are developed, which are then used in process simulations to identify the best operation conditions.

Comprehensive kinetic models, which contain often hundreds of species and thousands of reactions, are nowadays routinely generated with computer programs such as RMG (Green et al. 2013) and Genesys (Vandewiele et al. 2012). Such codes depend on reliable ways to calculate heavily the thermodynamic properties of all species encountered and rate coefficients for all possible reaction pathways. Because experimental data are generally scarce, and sophisticated first principle calculations too timeconsuming to be carried out for all reactions, group additivity based methods play a pivotal role in providing this thermochemical information.

The addition of H atoms or radicals to the aromatic ring followed by beta-scission to restore aromaticity is an important reaction sequence to change the substitution pattern of aromatic species. Therefore, automatically generated mechanism will contain this reaction class for all possible combinations of substituents and radicals. A systematic study of this family of reactions allows the development of group additivity values as introduced by Saeys et al. (2004). This enables assignments of rate parameters for any possible addition – elimination reaction involving monocyclic aromatic hydrocarbons.

Compared to the reactants, the transition state complex differs as a first approximation only in those moieties (groups) that undergo bond changes during the reaction. Neighboring groups to this reactive center have only an indirect impact on the reactivity. For the target reaction of this study, the reactive center comprises of the adding radical X as well as the aromatic ring, or, looking from the reverse reaction, the cycloheaxdienyl ring and the leaving X group. Substituents to the ring,



<sup>•</sup> To whom all correspondence should be addressed

Y and Z, should therefore only lead to marginal changes in reactivity. However, it is well known, that unsaturated substituents such as the vinyl or formyl groups markedly interact via resonance with the benzene ring (mesomeric effect) or resonantly stabilize radical sites. This might lead to stronger than usual non-nearest neighbor effects. One objective of this study is to address this question.

#### Methodology

The electronic structure calculations were performed at the CBS-QB3 level of theory (Montgomery et al. 1999) as implemented in the Gaussian 09 suite of programs. Electronic energies were converted to enthalpies with the atomization method (Curtiss et al., 1997). Since only relative energies are needed, no corrections to account for spinorbit couplings or systematic bond errors were applied. Well established methods from statistical mechanics were used to calculate entropies and heat capacities. Except for internal rotations around single bonds, internal modes were evaluated using the harmonic oscillator rigid rotor assumption. The frequencies were scaled by 0.99 prior to their use. Contributions from internal rotors were separately calculated by (a) determining for each rotation the hindrance potential via stepwise 10 degrees rotation around the bond, (b) calculating the reduced moment of inertia at the I<sup>3,2</sup> level as defined by East et al. (1997), (c) solving the 1dimensional Schroedinger equation using the free rotor wavefunctions as basis set, and (d) calculating the partition and contributions function for the thermodynamic properties for each rotor.

Canonical transition state theory was used to calculate the rate expressions within the temperature range 300 K - 2500 K in steps of 50 K. Tunneling corrections based on the asymmetric Eckart potential were applied.

As shown by Saeys et al. (2004), rate coefficients expressed in Arrhenius form for reactions that belong to the same reaction family can be cast in terms of contributions of the groups that form the reactive center ( $\Delta GAV^0(R_i)$ ) and corrections for non-nearest neighbor interactions ( $\Delta NNI_j^0$ ) if a suitable reference reaction is chosen.

$$E_a(T) = E_{a,ref}(T) + \sum \Delta GAV_{Ea,T}^0(R_i) + \sum \Delta NNI_{Ea,T,J}^0$$
$$\log_{10} \check{A}(T) = \log_{10} \check{A}_{raf}(T) +$$

$$\sum \Delta GAV_{logA,T}^{0}(R_{i}) + \sum \Delta NNI_{logA,T,j}^{0}$$

 $\check{A}(T)$  is the single event pre-exponential factor, which has to be multiplied by the number of event n<sub>e</sub> (also known as reaction path degeneracy) to obtain the total pre-exponential factor log<sub>10</sub>A.

$$n_e = \frac{n_{opt,\ddagger}}{\sigma_{\ddagger}} \frac{\sigma_{reac}}{n_{opt,react}}$$

'‡' refers to the transition state, '*reac*' to the total contributions from all reactants,  $\sigma$  is the total symmetry and  $n_{opt}$  the number of optical isomers.

#### Results

The effects of the groups X, Y, and Z (cf. *Scheme 1*) on the rate coefficients of radical addition reactions to substituted benzenes were studied in a sequential manner by separately analyzing the impact of each these substituents on the reactivity.

The importance of X. First, the influence of the nature of the adding radical was studied due to the expectation that variations in X will lead to the most severe changes in the reactivity. Rate coefficients for the addition of some 50 radicals X to either benzene (Y =H) or toluene (Y=CH<sub>3</sub>) were calculated. In Figure 1, the single event rate coefficients for a representative set of X adding to toluene are plotted against the inverse temperature. Distinct changes in reactivity are observed: H atoms add much faster to the aromatic ring than any carbon centered radical. Highly energetic vinyl and phenyl radicals react faster than sp<sup>3</sup>hydridized radicals, which in turn add faster to the ring than resonantly stabilized allyl, benzyl and propargyl radicals. Note that the formyl methyl radical (often called vinoxy) appears in the group of alkyl radicals. This suggests that, though it is formally resonantly stabilized, the formyl methyl Lewis structure dominates and the radical act as a substituted methyl radical rather than as a delocalized species.



Figure 1. Calculated single event rate coefficients for radical addition to toluene. A "#" in the names for X denotes a triple bond and "J" marks a radical site.

The impact of the leaving group X on the rate of the reverse  $\beta$ -scission reaction is shown in Figures 2 and 3. Figure 2 shows  $\beta$ -scission reactions that lead to the release of either a H atom or a carbon-centered radical. The elimination of H atoms or vinylic radicals is slowest, followed by methyl formation. Ethyl, hydroxymethyl are clearly easier formed than methyl, and the formation rate coefficient for t-butyl is of the same magnitude as those for the formation of resonantly stabilized radicals. It is important to notice that higher methyl substituted radicals are distinctly faster produced via  $\beta$ -scission than the corresponding primary radicals. Examples are benzyl vs phenyl isopropyl radical, propargyl vs 2-methyl but-3-yne-2-yl



Figure 2. Calculated single event rate coefficients for the  $\beta$ -scission reaction of X substituted 6-methylcyclohexa-2,4-dien-1-yl radicals to toluene + X. (see Figure 1 for naming conventions).

radical, and allyl vs 2-methyl but-3-ene-2-yl. Another important observation is that formyl radical is as easily released as resonantly stabilized radials and that the hydroxymethyl radical is faster produced than the methyl radical. The OH group in hydroxymethyl stabilizes this radical site and promotes its formation.

In Figure 3, the  $\beta$ -scission rate coefficients for important carbon-centered radials are compared to those for oxygen-centered radicals. Latter form three groups: (a) OH radical is formed with the slowest rate coefficient among all studied oxygen-centered radicals. Alkoxy radicals are more easily released with rate coefficients comparable to that for allyl radical. The bulkiness of the alkyl part has no notable impact on the rate coefficient. Finally vinoxy and phenoxy radicals are quickly formed and the calculated rate coefficients for these radicals are the highest among all  $\beta$ -scission reactions studied in this work, comparable only with highly methyl substituted allyl or benzyl radicals.

Similar trends are also observed for X addition

1.E+12  $Xcv(C(C)CJC=CC=C) => PhCH_{a} + X$ coefficient (s<sup>-1</sup>) 1.E+10 1.E+08 1.E+06 rate 1.E+04 event **B**-scission 1.E+02 1.E+00 - E1 C=CCI -CH3O 1.E-02 O ·CCO ·C2COI 1.E-04 single ·C3CO C=CO. 1.E-06 - PhO 1.E-08 0.5 1.5 2.5 x 10-1/T (K-1)

to benzene.

Figure 3. Calculated single event rate coefficients for the  $\beta$ -scission reaction of X substituted 6-methyl-

cyclohexa-2,4-dien-1-yl radicals to toluene + X. The formation of oxygen-centered radicals X is compared with common carbon centered radicals and H atom.

The wide range of activation energies and enthalpies of reaction become obvious in Evans-Polanyi plots (Ea versus  $\Delta_{\rm R}$  H), as demonstrated in Figure 4 for the  $\beta$ scission of substituted methyl cyclohexadienyl radicals forming toluene and the carbon-centered radical X. The colors are chosen to easily distinguish between resonantly stabilized (allyl, benzyl, propargyl, allenyl) (green), alkyl (black), carbonyl (yellow), vinyl (brown) and phenyl (orange) radicals. Note that the carbonyl group forms two sub-groups, one comprising of  $R(H)C \bullet (=O)$  radicals and the second one of  $C\bullet(=O)OR(H)$ . One phenylic radical is an outlier: 2,6dimethyl phenyl radical. Upon reacting with toluene it forms an unstable adduct due to steric interactions. This is reflected in the unusual decomposition kinetics. Despite some scatter, all data follow reasonably well a linear dependency with a slope of 0.6 suggesting that the transition state is more or less half-way between the reactants and products.



Figure 4. Activation energies for the  $\beta$ -scission of X substituted methylcyclohexadienyl radicals to toluene and plotted against the enthalpies of reaction. All X are carbon-centered radicals. (see text)

The importance of Y. The impact of a substituent Y at the ipso position of the ring on the addition reaction was studied by calculation the rate coefficients for H or CH<sub>3</sub> addition to the Y substituted ring carbon. Some 50 different Y groups were considered. The results show that the addition reaction is rather independent of the Y substituent (see Figure 5). A closer look at the



Figure 5. Calculated single event rate coefficients for

*H* addition to *Y* substituted benzenes. The reactions are classified in terms of the nature of the site to which the *H* atom adds.

thermochemistry revealed that Y substituents alter the heat of reaction only little (the highest and lowest heats of reaction differ in the H atom addition reaction by approximately 20 kJ/mol) and the activation energy differences were even less.

The importance of Z substituents. Finally, calculations were performed to study the impact of substituents in ortho, meta or para position to the site to which H atoms or methyl radicals added. As in the case of Y substituents, only small deviations between the calculated rate expressions were observed. For example, all nine rate coefficients for H addition to methyl, hydroxyl or formyl substituted benzenes (either in o-, m-, or p- position) agree to a factor of two at 1000 K. A more comprehensive study involving substituent pairs (Y,Z) that are known to cause strong non-nearest neighbor interactions is currently in progress.

#### Discussion

The most important result is that the radical addition kinetics to monocyclic aromatic molecules is mainly determined by the nature of the adding radical and to a much lesser extent by substituents attached to the ring. This provides an easy means to calculate the rate coefficients by simply applying corrections to the logarithms of the pre-exponential factor and to the activation energy of a chosen reference reaction (e.g., CH3 + toluene). Rate coefficients of reaction that have a crucial impact on the accuracy of model predictions can easily be further improved by applying  $\Delta NNI_{j}^{0}$  corrections to account for the minor Y and Z effects.

A second important result is the reactivity order seen for the  $\beta$ -scission reaction. H and CH<sub>3</sub> are formed at a slower rate than for example CH<sub>2</sub>OH, OH or secondary and tertiary alkyl radicals. This means that at reaction conditions with a sufficiently large H and methyl radical pool, benzene and toluene should be easily formed in secondary reactions, while bulky substituents disappear. This is in accordance with observations in biomass pyrolysis experiments, which show that the fraction of benzene increases with reaction time (or temperature) while other aromatic species are consumed (Jablonski et al. 2009).

#### Conclusions

Radical addition reactions to substituted benzenes and the reverse reactions have been studied at the CBS-QB3 level of theory and the observed trends have been analyzed. The reactivity is mainly determined by the nature of the adding radical while substituents in ipso-, ortho-, meta- or para-position only have small impacts. Similarly, the rate of the reverse  $\beta$ -scission reaction is large determined by the

nature of the leaving radial. Reactivity changes of several orders of magnitude were found, in particular at lower temperatures. The results can easily be implemented in the  $\Delta GAV^0$  group additivity scheme developed by Saeys et al. (2004) which is used by the automated mechanism generation software Genesys to calculate rate coefficients for unknown reactions.

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## AB INITIO QUANTUM CHEMICAL REACTION KINETICS: RECENT APPLICATIONS IN COMBUSTION CHEMISTRY

Ghanshyam L. Vaghjiani,\* Hongyan Sun and Steve D. Chambreau Air Force Research Laboratory, AFRL/RQRP, Edwards AFB, California 93524, USA

Keywords: Ab initio Quantum Chemistry, Reaction Kinetics, Propellant Combustion

High-level *ab initio* quantum chemical computations have been carried out to provide detailed and accurate information on the potential energy surface(s), chemical mechanism(s) and the reaction kinetics involved in the combustion of a number of propellant systems. Such calculations are the only method available when experimental data is unobtainable because of limitations in probing the systems under extreme conditions of high temperatures and pressures. On the other hand, they can be complementary to and or used to validate experimental data when available.

Mononitrobiuret (MNB) and 1,5-Dinitrobiuret (DNB) are, tetrazole-free, nitrogenrich, energetic compounds. The potential energy surface for thermal decomposition of MNB was characterized at the RCCSD(T)/cc-pV $\infty$ Z//M06-2X/aug-cc-pVTZ level of theory. It was found that the thermal decomposition of MNB is initiated by the elimination of HNCO and HNN(O)OH intermediate. Intra-molecular transfer of an H-atom, respectively, from the terminal NH<sub>2</sub> group to the adjacent carbonyl O-atom via a six-member-ring transition state eliminates HNCO with an energy barrier of 35 kcal/mol, and from the central NH group to the adjacent nitro O-atom eliminates HNN(O)OH with an energy barrier of 34 kcal/mol. Elimination of HNN(O)OH is also the primary channel involved in the thermal decomposition of DNB, which processes a C<sub>2v</sub> symmetry.



Potential energy surface for the decomposition of MNB calculated at the RCCSD(T)/cc- $pV\infty Z//M06-2X/aug-cc-pVTZ$  level of theory.

The rate coefficients for the primary decomposition channels for MNB and DNB were quantified as functions of temperature and pressure. The present theoretical results can be used to successfully interpret previously reported experimental results of Klapötke et al. (Combust. Flame, **2004**, *139*, 358-366) regarding the thermal instability of DNB and its decomposition products. In addition, the thermal decomposition of HNN(O)OH was analyzed via RRKM/multi-well master equation simulations, the results of which reveal (N<sub>2</sub>O + H<sub>2</sub>O) to be the major decomposition products. The present study provides a fundamental understanding of the stability of the molecular structures of nitrobiurets and their key reactions leading to ignition.

The N<sub>2</sub>H<sub>3</sub>-radical reaction with NO<sub>2</sub> was studied theoretically and experimentally. The potential energy surface was investigated by *ab initio* multi-reference second-order perturbation, density functional, quadratic configuration interactions, and coupled-cluster theories. The reaction proceeds via a complex mechanism with submerged energy barriers and relatively large exothermicities. Direct NO<sub>2</sub> addition to the NH site in N<sub>2</sub>H<sub>3</sub> forms two isomeric adducts. The isomeric adducts undergo decomposition to trans-HONO + trans-NH=NH and trans-HONO + cis-NH=NH. Furthermore, the addition adducts undergo decomposition to NO, NNH and H<sub>2</sub>O via several steps involving isomerization and molecular elimination.



# Potential energy surface for the NO<sub>2</sub> + N<sub>2</sub>H<sub>3</sub> system involving the formation of the N<sub>2</sub>H<sub>3</sub>NO<sub>2</sub> adduct. Energies are zero-point corrected and relative to that of entrance channel at 0 K.

Also, NO<sub>2</sub> can add to the NH<sub>2</sub> site in  $N_2H_3$  to form an unstable adduct which undergoes isomerization to form the NH<sub>2</sub>NHONO isomer. Important reaction channels for the NH<sub>2</sub>NHONO isomers involve dissociation to NO + NH<sub>2</sub>NHO radical products.

The reaction kinetics of  $N_2H_3$  in excess  $NO_2$  was studied in 2 Torr of  $N_2$  and 298 K in a pulsed photolysis flow-tube reactor. Upon laser photolysis of  $N_2H_4$ , the reacting gas was

mass spectrometrically sampled using a skimmer as the mixture escaped via a pin-hole inside the flow-tube reactor. The temporal profile of the product, HONO, was determined by direct detection of the m/z = 47 ion signal. For each chosen [NO<sub>2</sub>], the observed [HONO] trace could be fitted to a bi-exponential kinetics expression, which yielded a value for the pseudofirst-order rate coefficient, k', for the reaction of N<sub>2</sub>H<sub>3</sub> with NO<sub>2</sub>. The slope of a plot of k' versus [NO<sub>2</sub>] yielded a value for the bimolecular rate coefficient,  $k = (1.23 \pm 0.25) \times 10^{-11}$ cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Pressure-dependent rate coefficients of the N<sub>2</sub>H<sub>3</sub> + NO<sub>2</sub> reaction were determined by RRKM theory with multi-well master equation simulations. With  $\Delta E_{down} = 100 \times (T/300)^{0.85}$  cm<sup>-1</sup> for the energy transfer probability, excellent agreement was observed between the measured value and the computed overall rate coefficient at 298 K and 2 Torr of N<sub>2</sub>.



# Reaction rate coefficients for various product channels (as well as the high pressure limit) as a function of temperature, and the overall $k_{298K}$ experimental value in 2 Torr of N<sub>2</sub> for N<sub>2</sub>H<sub>3</sub> + NO<sub>2</sub>.

The negative energy barriers and large exothermicities for the various product channels suggest a significant role of this reaction in the early stages of hypergolic ignition of hydrazine and its derivatives.

<sup>\*</sup> Corresponding author email: <u>ghanshyam.vaghjiani@us.af.mil</u>

### RATE CONSTANTS FROM ELEMENTARY REACTIONS MAY FAIL FOR COMBUSTION KINETICS MODELS

João Brandão\* and César Mogo CIQA - Centro de Investigação em Química do Algarve Universidade do Algarve, Faro, Portugal

#### Abstract

Kinetics models use available kinetic data, rate constants and their variation with temperature to model complex mechanisms and have been successfully applied to model combustion processes. They rely on the assumption that the number of collisions between reactants and intermediates is large enough to achieve thermal equilibrium. Preliminary results of a theoretical study on the behaviour of the OH radical during the combustion of an equimolecular mixture of oxygen and hydrogen show a non-thermal distribution of the internal energy of intermediate radicals, in spite of the occurrence of a large number of collisions which are more efficient in rotational and translational energy transfer than in vibrational quenching. As a consequence, the OH radical has shown to be vibrationally excited, having an average energy which is twice the rotational.

#### Keywords

Reaction dynamics, Hydrogen combustion, Energy distribution, Non-thermal equilibrium, Computer modelling.

#### Introduction

Although simple when compared with other combustion processes, the combustion of hydrogen in the presence of oxygen is a rather complicated process. It involves a large number of reactions with reactants in different electronic states. Such a complex mechanism is usually treated by kinetic models, which use available thermal rate constants and thermochemistry information to integrate the differential equations.

Once defined the chemical reactions to include in the reaction mechanism, the main problem is the determination of the rate constants of the elementary reactions and their variation with the temperature.

The study of each elementary reaction is often a difficult experimental task. Frequently, these reactions involve radicals, chemical species with unpaired electrons, which are very reactive and difficult to isolate. One of the most commonly used techniques, molecular beams, gives a strong insight of the reaction dynamics and energy distribution of the products but, due to experimental design, it cannot give absolute values for the rate constants.

On the other hand, theoretical studies of these reactions are nowadays feasible with growing accuracy. A vast number of Potential Energy Surfaces (PESs) for the ground and first excited states of small systems are now available with chemical accuracy. By using those PESs, it is now possible to compute the thermal rate constants at different temperatures with great precision. In Figure 1, we present a comparison of theoretical and experimental thermal rate constants for the reaction of O ( $^{1}$ D) + H<sub>2</sub>. There we can see the



<u>ibrandao@ualg.pt</u> To whom all correspondence should be addressed.

Figure 1. Comparison between experimental and theoretical values for the rate constant of the reaction  $O(^{1}D)+H_{2}$ , including the role of excited surfaces. represents the estimated rate constant using the BR PES (Brandão and Rio, 2003). Most recent experimental data:  $\Delta$ , NASA report (Sander et al., 2006); •••••• and  $\circ$ , (Altkinson et al., 1992) and  $\diamond$ (Talukdar and Ravishankara 1996).

excellent agreement between theory and experiment and the non-Arrhenius behaviour of this elementary reaction.

Despite these results, a large amount of the most accurate kinetic model studies of combustion reactions use rate constants fitted from experimental combustion data, and a lot of work is still going on in this direction.

Thermal rate constants assume that reactants in the bulk mixture are in thermal equilibrium, *i.e.*, their translational, rotational and vibrational energy is distributed according to a Boltzmann distribution at the same temperature for all the degrees of freedom of the molecular system. Assuming this, thermal rate constants are an average of state to state reaction probabilities weighted by their Boltzmann distributions.

In contrast, the energy distribution of the products of a reaction is ruled by the conservation laws of energy, linear and angular momentum and strongly depends on the dynamics of the reaction. Theoretical studies have shown that the reaction energy will be recovered as translational, vibrational or rotational energy according to the position of the energy barrier, the insertion or abstraction mechanism of the reaction, and the reactive complex lifetime. In most of the cases, even when statistical theories can be applied, the energy distribution of the products is far from the Boltzmann distribution. In Figures 2, 3 and 4, we display the translational, rotational and vibrational energy distribution of the H + OH products of the above referred reaction (Rio and Brandão, 2007). In those figures we can see that, in this exothermic reaction, none of the energy distribution has a Boltzmannian shape and that the temperature that best fits those distributions is different for each type of energy. We can also see the good agreement between the quasiclassical trajectory results and experiment.



Figure 2. Translational energy distribution of the products of the reaction  $O({}^{1}D)+H_{2}$ .—trajectory ---- and statistical results (Rio and Brandão, 2007); ---- and shadow area experiment (Alagia et al., 1998); the line - - - represents a coarse fit to a Maxwell-Boltzmann distribution.

It is well known that thermalization, i.e. the exchange of energy in order to achieve a random

distribution, mainly occurs by energy transfer during the collisions between the different molecular species present in the bulk mixture, see e.g. Levine and Jortner (1976). This energy transfer strongly depends on the mass and forces between the colliding partners.



Figure 3. Rotational energy distribution of the products of the reaction  $O({}^{1}D)+H_{2}$ . Lines as in Fig. 2.



Figure 4. Vibrational energy distribution of the products of the reaction  $O({}^{1}D)+H_{2}$ . Lines as in Fig. 2.

In a gas phase combustion or explosion, reactants and intermediates can be far from thermal equilibrium, i.e., the number of non-reactive collisions can be small and the energy distribution of the intermediate species will be far from the Boltzmann distribution, depending on the energy distribution at the time of their formation and on the energy transfer in the non-reactive collisions. The energy distribution of the different species will have an effect on the overall reaction rate.

#### Calculations

As stated above, the Potential Energy Surfaces (PESs) based on ab initio calculations are a powerful tool to theoretically study the rate of elementary reactions and their dynamics, being useful to compute state to state rate constants. In a more complex mechanism such as a combustion process, we will be in the presence of different and simultaneous elementary reactions, corresponding to all the possible reactive and non-reactive collisions between the different species present and leading to the respective products. Attempting to build a traditional PES for such a system easily becomes an impossible mission.

Recently, we proposed a method to model complex reactive systems incorporating accurate PESs, reactive and nonreactive, and concurrently integrating the equations of motion of the chemical species present in the bulk (Mogo and Brandão, 2014). This is accomplished by defining a global Potential Energy Surface (gPES) integrating various PESs, each one of them representing an elementary reaction that is expected to play a role in the chemical process. Multiprocess Reaction Dynamics, MReaDy, is a program that builds an overall PES for the process in question and performs reactive classical dynamic calculations on it. Starting from a bulk mixture of  $H_2$  and  $O_2$ molecules, the program integrates the equations of motion in a total potential built from 17 accurate potential energy surfaces such as H<sub>4</sub>, H<sub>3</sub>O, HO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> or H<sub>2</sub>O (singlet and triplet states) among others that should play a role in the combustion process. The overall results of this calculation have shown to be in reasonable agreement with similar kinetic model results (Mogo and Brandão, 2014).

To test the distribution of the reaction partners, we have followed the evolution of the hydroxyl radical in its ground electronic state, OH ( $2\Pi$ ), which is an important and very reactive intermediate during the combustion of a equimolecular mixture of oxygen and hydrogen, started at 3000 K and 2 atm, until 2 ns, using the MReaDy program.

To follow the OH radical, the MReaDy program has been modified in order to print out the identification, the position and the velocity of each O and H atom of a OH radical, every time a OH radical is "formed" or "consumed". By "formed" we mean that it comes out of a collision, and by "consumed" that it starts a new collision. Using this information, we have been able to decompose the kinetic energy in its translational and intramolecular components, allowing us to assign the rotational and vibrational quantum numbers.

We are aware that we are using classical mechanics to simulate a process that should be treated rigorously by using quantum mechanics. Despite that, studies in reaction dynamics and molecular energy transfer have shown that classical mechanics gives reasonable accurate results and allows us to study the details of chemical processes at high temperatures, such as combustion processes.

#### **Results and Discussion**

In this work we present preliminary results of the study referred above.

In Table 1, we present the predicted distribution of energy of the radical OH computed using the molecular

partition functions and spectroscopic information of the radical.

Table 1. Predicted statistical distribution of the energy.

Temperature		Translational	Rotational	Vibrational
1 000 K	Energy / J	0.2071E-19	0.1381E-19	0.3752E-19
1 000 K	Fraction	0.2875	0.1916	0.5201
2 000 K	Energy / J	0.6213E-19	0.4142E-19	0.5199E-19
3 000 K	Fraction	0.3994	0.2663	0.3342
5 000 V	Energy / J	1.0355E-19	0.6903E-19	0.7558E-19
5 000 K	Fraction	0.4173	0.2782	0.3045
7.000 K	Energy / J	1.4497E-19	0.9665E-19	1.0136E-19
7 000 K	Fraction	0.4227	0.2818	0.2955
0.000 K	Energy / J	1.864E-19	1.2426E-19	1.2794E-19
9 000 K	Fraction	0.4250	0.2833	0.2917

In this table we can see that at 1 000 K the vibrational energy is close to 50% of the total energy. This is due to the high zero point energy of this radical. We also see that the translational energy comes close to 1.5 times the rotational at all the temperatures. At higher temperatures the rotational and vibrational temperatures approach each other, and at very high temperatures the partition of the total energy approaches 1.5:1:1, in agreement with the principle of the equipartition of the energy for a diatomic, which has 3 degrees of freedom for the translation, 2 degrees of freedom for the 1 mode vibration.

Using the procedure above described we have been able to follow each OH radical since the moment it was formed until it was consumed to give products. We have information about all its collisions and the energy transfer in each encounter. However, in this work we are only interested in the statistical behavior of these radicals and we present in Table 2 a summary of our preliminary results at two different circumstances.

Table 2. Observed energy distribution.

Computed		Translational	Rotational	Vibrational
Formation	Energy / J Fraction	0.3511E-19 0.2326	0.4147E-19 0.2748	0.7436E-19 0.4926
2 ps	Energy / J	0.5158E-19	0.5110E-19	1.0280E-19
~100 collis.	Fraction	0.2510	0.2487	0.5003

The first two lines refer to an average of the energy distribution of the OH radicals at the time they are formed. They have no physical meaning because they are formed at different times during the combustion procedure and the bulk energy is increasing with time. Even so, we can see that this radical is formed with a rotational energy higher than the translational energy and an even higher vibrational energy. If we compare the average energies with the values quoted in Table 1, we should assign the temperatures of 2000 K, 3000 K and 5000 K to the translational, rotational and vibrational energies, respectively.

The last two lines refer to the energy distribution of the OH radicals present in the bulk mixture after 2 ns of reaction time. Some radicals have already reacted to form products, but others are still present or recently formed. Looking at the history of the different OH radicals we can say that they have undergone an average of 100 non-reactive collisions. Some have experienced 50 and a few about 180 collisions. These two lines show that the average total energy of the OH radical has increased when compared with its formation. This should be a result of the energy released in the overall chemical process. We can see, however, that the rotational energy is now equal to the translational, but the average vibrational energy is still twice the average value of the other two components. Comparing with the average values quoted in Table 1, marked in bold, we can assign the temperatures of 3000 K, 5000 K and 7000 K to the translation, rotational and vibrational energies, respectively. In Figure 5 we compare the present results for the vibrational energy with the expected Boltzmann distribution at 3000 K and 8000 K. There we can see that higher temperature best agrees with our results.

These results show that non-reactive collisions can increase the overall energy of the system, due to the higher kinetic energy available in the system. They also show that the transference of translational energy is somehow more efficient than the transference of rotational energy, as it should be expected due to the above referred larger number of degrees of freedom of the translation. In regard to the vibrational energy, the collisions keep its value at 50% of the total energy. As



Figure 5. Comparison of the OH vibrational distributions. — theoretical prediction; Boltzmann distributions: … at 3 000 K and - - - at 8 000 K.

a consequence, the OH radical seems to be vibrationally excited, having an average energy which is twice the rotational or translational.

These theoretical result agrees with early spectroscopic studies on hydrogen-oxygen flames (Broida and Shuler, 1952) as well as with recent shock tube experiments (Skrebkov et al., 2009, Skrebkov, 2014).

#### Conclusions

This theoretical study has shown that the energy distribution of the OH radical in a combustion process of a hydrogen-oxygen mixture is far from thermal equilibrium. Our preliminary results show that the radical OH is highly excited in regard to the vibrational energy. In addition, the rotational and translational temperatures are not the same.

As a consequence we cannot define a rate constant for the reactions involving this radical as reactant. The use of theoretical or experimental thermal rate constants for these elementary reactions should be avoided, and fitted rate constants should be used instead. However, they should be considered as "effective" but not "real" values.

As the number of non-reactive collisions should depend on the temperature and composition of the mixture, the energy distribution in the OH radical should depend on the reaction conditions. As a result, thermal rate constants fitted for one experiment may not be suitable for very different conditions.

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## **REACTIONS OF NH2 WITH FORMALDEHYDE, HYDROGEN PEROXIDE AND HYDRAZINE: A CHALLENGE TO THEORY**

Yide Gao and Paul Marshall\* University of North Texas Denton, TX 76203

#### Abstract

The pulsed laser photolysis / laser-induced fluorescence method has been used to generate amidogen radicals from  $NH_3$  precursor at 193 nm. Time-resolved LIF measurements were made on three reactions of  $NH_2$ , with  $CH_2O$ ,  $H_2O_2$  and  $N_2H_4$ , to obtain

$k(NH_2+CH_2O) = 7.8 \times 10^{-12} exp(-18.6 kJ mol^{-1}/RT) cm^3 molecule^{-1} s^{-1}$	(T = 294-643  K)
$k(NH_2+H_2O_2) = 2.4 \text{ x } 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	(T = 412 K)
$k(NH_2+N_2H_4) = 5.4 \text{ x } 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	(T = 296 K)

None of these rate constants have been isolated experimentally before. Prior and apparently reliable *ab initio* analyses in the literature are shown to be in error by orders of magnitude. The reasons for this are discussed in the context of potential energy surfaces based on our own new calculations.

#### Keywords

NH<sub>2</sub>, potential energy surface, CH<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub>, N<sub>2</sub>H<sub>4</sub>

#### Introduction

Amidogen (NH<sub>2</sub>) radicals are key combustion intermediates whose oxidation yields NO<sub>x</sub>. Further reaction with NH<sub>2</sub> can recycle NO back to N<sub>2</sub>, which is the basis of selective non-catalytic reduction of NO<sub>x</sub> in exhaust gases. Many reactions of NH<sub>2</sub> with other molecular flame and atmospheric species such as O<sub>2</sub> and hydrocarbons are fairly slow. In the atmosphere, NH<sub>2</sub> can be formed by NH<sub>3</sub> photolysis or abstraction of H by OH. NH<sub>2</sub> might also play a role in astrochemistry.

Here we present results from kinetic studies of  $NH_2$  with three molecules with weak bonds to hydrogen, so that moderate reactivity was expected. This is in contrast to published *ab initio* computational studies, which predicted very low reactivity near room temperature (Li and Lü, 2002, Li and Zhang, 2006). These discrepancies are discussed, with emphasis on the possibilities of multiple reaction paths and the role of internal rotation in the transition states.

#### Methodology

Our experimental set up has been described elsewhere (Gao and Marshall, 2014). Briefly,  $NH_2$  is generated by 193 nm photolysis of  $NH_3$  and monitored during pseudo-first-order decay by laser-induced fluorescence at 570.3 nm. Evaluation of the decay rate

as a function of added reactant (CH<sub>2</sub>O,  $H_2O_2$  or  $N_2H_4$ ) yields the bimolecular rate constant. The reactant concentration was verified via UV absorption, and experimental parameters such as the photolysis energy and residence time were varied to ensure the elementary reactions were isolated from secondary chemistry.

#### **Results and Discussion**

The following rate constants were determined:

 $k(NH_2+CH_2O)=7.8\ x\ 10^{-12}\ exp(-18.6\ kJ\ mol^{-1}/RT)\ cm^3\ molecule^{-1}\ s^{-1}\ over\ 294-643\ K$ 

 $k(NH_2+H_2O_2) = 2.4 \text{ x } 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 412 \text{ K}$ 

 $k(NH_2+N_2H_4) = 5.4 \text{ x } 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 296 \text{ K}$ 

Potential energy surfaces were investigated computationally for the three reactions to explain their unexpectedly fast kinetics. In the case of  $NH_2 + CH_2O$ a new reaction path leading to formamide (HCONH<sub>2</sub>) is proposed. The impact of rotational conformations is explored in these systems.

#### Conclusions

Consideration of experimental data for the title reactions drove further computational analysis and

<sup>•</sup> To whom all correspondence should be addressed

together these approaches yield an improved understanding of  $NH_2$  chemistry.

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## Direct Dissociation of Excited Radicals is Important in Combustion Modeling

Nicole J. Labbe, Raghu Sivaramakrishnan, Franklin C. Goldsmith,<sup>#</sup> James A. Miller, Stephen J. Klippenstein

Chemical Sciences & Engineering Division, Argonne National Laboratory, Argonne, IL-60439. <sup>#</sup> School of Engineering, Brown University, Providence, RI-02912.

#### Keywords

#### Combustion kinetics, excited radicals, HCO, non-Boltzmann, flame speed

In combustion and atmospheric chemistry, the decomposition of radicals (formed by either unimolecular or bimolecular reactions) is almost always assumed to be characterized by thermal kinetics; i.e. the internal states of the radical are equilibrated according to a Maxwell-Boltzmann distribution, which is established via a sequence of inelastic collisions with an inert 3<sup>rd</sup> body prior to dissociation or subsequent reaction. The present work calls into question the justifiability of this assumption. We present theoretical studies on the kinetics of the formyl radical, HCO, which is an important intermediate species in combustion and is typical of weakly bound radicals. At combustionrelevant temperatures (e.g. T > 1000 K), a substantial percentage of the Boltzmann population of states lies near or above the HCO dissociation threshold. Under these conditions, a significant fraction of the HCO produced in any reaction will dissociate directly to H + CO. Consequently, the phenomenological rate coefficients for elementary reactions that produce HCO should include a branching fraction for producing H + CO as well. This effect is exacerbated when HCO is formed as co-product in an exothermic reaction. For these reactions, which account for the majority of reactions that produce HCO, an additional amount of the ro-vibrationally excited HCO will dissociate prior to thermalization. To quantify this latter effect, direct dynamics calculations were performed for the  $CH_2O + OH \rightarrow HCO + H_2O$  reaction. The energy distribution predicted from the direct dynamics calculations is coupled directly into Master Equation (ME) simulations to predict the fraction of the incipient HCO that directly dissociates.

The preceding analysis has been incorporated into numerical simulations of flame propagation, ignition, and species formation for simple hydrocarbons and oxygenated fuels – CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and CH<sub>3</sub>OH – using two popular chemical kinetic mechanisms taken from the literature. For each mechanism, four separate simulations were performed. In the first case, each system was modeled using the mechanism "as is" as a reference case. In the second simulation, all reactions that produce HCO where modified to include a branching fraction for H + CO that is predicted by the non-equilibrium factor,  $f_{ne}$ , which is a measure of the degree to which direct dissociation perturbs the equilibrium distribution of states; this simulation is considered the lower limit for the effects of direct dissociation. In the third simulation, the branching fraction to H + CO is obtained from a statistical energy partitioning to the HCO co-product; this simulation is considered the upper limit. The fourth simulation incorporates the energy distribution predicted from the direct dynamics / ME calculations.

These simulations indicate that the direct dissociation of radicals has a profound influence on the prediction of combustion properties. Non-equilibrium effects, especially for weakly bound radicals (e.g. HCO, C<sub>2</sub>H<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, CH<sub>2</sub>OH), need to be characterized for combustion and atmospheric chemistry. The present work also suggests that the vast majority of prior experimental characterizations of HCO kinetics at combustion temperatures needs to be revisited to account for prompt dissociation.

## Thermochemical Properties for Cyclopentadienone- Alcohols, Hydroperoxides, Vinylic, Alkoxy and Alkylperoxy Radicals: Cyclopentadienone-yl + O2 Kinetics

Suriyakit Yommee and Joseph W. Bozzelli\*

Department of Chemistry and Environmental Science, New Jersey Institute of Technology University Heights, Newark, NJ 07102 USA

#### Abstract

**Abstract**: Cyclopentadienone has two olefin groups and one carbonyl contributing 4n + 2 pi electrons in a cyclic five member ring structure. Thermochemical and kinetic parameters for the initial reactions of cyclopentadienone radicals with O<sub>2</sub> and the thermochemical properties for cyclopentadienone - hydroperoxides, alcohols, alkenyl, alkoxy and peroxy radicals have been determined by use of computational chemistry. The CBS-QB3 composite and B3LYP density function theory methods were used for enthalpies of formation ( $\Delta_{f}H^{o}_{298}$ ) using the isodesmic reaction schemes with several work reactions for each species. Entropy and heat capacity,  $S^{\circ}(T)$  and  $C_{P^{\circ}}(T)$  (50 K  $\leq$  T  $\leq$  5000 K) are determined using geometric parameters, internal rotor potentials, and frequencies from B3LYP/6-31G (d,p) calculations. Standard enthalpies of formation are reported for parent molecules as cyclopentadienone, and cyclopentadienone with alcohol, and hydroperoxide substituents, and for the cyclopentadienone-yl vinyl, alkoxy, and peroxy radicals corresponding to loss of a hydrogen atom from the carbon and oxygen sites. Entropy and heat capacity vs. temperature also are reported for the parent molecules and for radicals corresponding to loss of H atom from carbon and oxygen sites. The thermochemical analysis shows the R + O<sub>2</sub> reactions to RO + O (chain branching products) for cyclopentadienone-2-yl and cyclopentadienone-3-yl have unusually low reaction (AHrxn) enthalpies, some 20 or so kcal/mol below that of the cyclopentadienyl radicals plus O<sub>2</sub>. The R• + O2 well depths are deep, on the order of 50 kcal mol<sup>-1</sup>. Chemical activation kinetics using quantum RRK analysis for k(E) and master equation for fall-off are used to show importance chain branching as a function of temperature and pressure

Keywords Thermochemistry, Bond Dissociaiton Energies, Oxidation Kinetic, Chain Branching

#### Introduction

Cyclopentadienone has a 4n + 2 pi electron configuration similar to that of benzene and furans and reactions of the ring radical sites appear to undergo chain branching to a more significant extent than vinyl radicals or phenyl radicals<sup>1-2</sup>. Evaluation of its thermochemistry shows a strong effect of the carbonyl group on the ring vinyl carbons, their thermochemistry and the effects of alcohol and hydroperoxy groups and on C-H bond dissociation energies. It is of value to understand these effects and the changes in the vinyl carbon reactions under thermal and combustion conditions. To our knowledge no one has studied the extensive thermochemistry or kinetics of these oxygenated derivatives and corresponding radicals.

In an early study Zhong and Bozzelli<sup>3</sup> carried out the study thermochemistry and kinetic analysis with thermochemical known reactants, intermediates, and product species with evaluations based on literature data and group additivity contributions with available hydrogen bond increments; they estimated  $\Delta_{f}H^{o}_{298}$  of cyclopentadienone at 7.4 kcal mol<sup>-1</sup>. The  $\Delta_{f}H^{o}_{298}$  of cyclopentadienone was subsequently calculated by Wang and Brezinsky<sup>1</sup> at 13.2 kcal mol<sup>-1</sup> using ab initio molecular orbital calculations at the G2(MP2,SVP) and G2(B3LYP/MP2,SVP) levels of theory and with the use of isodesmic reactions. In a separate study the heat of formation data of cyclopentadienone (12.75 kcal

mol<sup>-1</sup>) was calculated by Robinson and Lindstedt in 2011<sup>4</sup>, where the kinetic and thermochemical parameters were calculated using G4/G4MP2 and G3B3 composite methods. Linstedt also obtained the equilibrium structure from B3LYP with the 6-31G (2df,p) basis set and determined the thermochemical data relative to the oxidation reactions of the cyclopentadiene and oxygenated cyclopentadienyl intermediates.

In 2014, Ormand et al<sup>5</sup> used flash pyrolysis of ophenylene sulfite (C6H4O2SO) to provide a molecular beam of cyclopentadienone (for collection by matrix isolation. The products were confirmed via photoionization mass spectroscopy (PIMS) and infrared. They reported on its symmetry and vibration frequencies, which were further validated with al<sup>6</sup> calculations. Scheer et reported that cyclopentadienone is detected and confirmed by IR spectroscopy as an intermediate in a unimolecular decomposition of methoxyphenols. Cyclopentadienone can react to form radicals from loss (abstraction) of hydrogen atoms, and these alken-yl radicals will react with O<sub>2</sub> to form peroxy and alkoxy radicals at the different sites on the ring. The radicals can also undergo ring opening to reactive, unsaturated noncyclic species via thermal processes.

Thermochemical properties: formation enthalpies  $(\Delta_{\rm f} H^{\rm o}_{298})$ , entropies (S°), heat capacities (C<sub>P</sub>°(T)), and bond dissociation enthalpies (BDEs) for the vinylic
carbon radicals and the corresponding hydroperoxides, peroxy radicals, alcohols and alkoxy radicals of cyclopentadienone are needed to understand reaction paths and to assist in developing the chemical kinetic mechanisms. Ab initio composite and Density Functional Theory methods were used with work reactions to calculate the thermochemical properties for of these target molecules and radical intermediates and kinetic parameters for ring opening reactions of the vinylic radicals and the R + O2 initial reaction steps. Results show the  $R + O_2$  association reactions to have an unusually deep well (~50 kcal mol<sup>-1</sup>) relative to ~ 46 in the vinyl and phenyl +  $O_2$  systems. Furthermore the chemical activation reactions of R• +  $O_2$  to  $RO \bullet + O$  atom (chain branching) for the cyclopentadienone -2-yl and 3-yl carbon radicals have significantly lower reaction enthalpies. The kinetic analysis in this study suggests that the  $R + O_2$  chain branching reaction to RO + O is an important path in the cyclopentadienone vinyl radical reactions with molecular oxygen under combustion conditions and to some extent under atmospheric conditions.

## **COMPUTATIONAL METHODS**

The structures of cyclopentadienone and the corresponding alcohols, hydroperoxides, and radicals corresponding to the loss of H atoms, plus standard enthalpies of formation for the parents and radicals have been calculated using B3LYP hybrid density functional theory in conjunction with the 6-31G(d,p)<sup>7-8</sup> basis set and the composite CBS-QB3 level of theory<sup>9</sup>. All quantum chemical calculation has been performed within the Gaussian 03 and 09 suites of programs.

#### Scheme 1 nomenclature for radical and functional group sites



Standard Enthalpies of formation ( $\Delta_t H^{o}_{298}$ ) To more accurately evaluate the standard enthalpy of formation ( $\Delta_f H^{o}_{298}$ ), a variety of homodesmic and isodesmic work reactions have been used to calculate the standard enthalpy of formation for both parent molecules and radicals at each level of theory. An isodesmic reaction is a hypothetical reaction where the number and type of bonds is conserved on each side of the work reaction, and a homodesmic reaction conserves number and type of bonds, but also conserves hybridization<sup>10</sup>. The thermal enthalpy of each species in the work reaction is determined, which allows calculation of  $\Delta_f H^{o}_{298}$ reaction. The known  $\Delta_f H^{o}_{298}$  values of the three reference molecules are used with the calculated  $\Delta_{\rm f} H^{\rm o}_{298}$  reaction to determine the standard enthalpies of formation. The use of similar structural components on both sides of the work reaction provide a cancellation of systematic errors that may exist in the calculation of  $\Delta_{\rm f} H^{\rm o}_{298}$  for each species and allows for an increase in accuracy for the standard enthalpy analysis.

## Structures

Table 1: Structure and abbreviated nomenclature of the stable molecules

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y(c5h4do) cyclopentadienone	y(c <sub>5</sub> h <sub>3</sub> do)oh2 2-hydroxyl cyclopentadienone	y(c5h3do)oh3 3-hydroxyl cyclopentadienone	y(c <sub>5</sub> h <sub>3</sub> do)q2 2-hydroperoxy cyclopentadienone	y(c <sub>3</sub> h <sub>3</sub> do)q3 3- hydroperoxy cyclopentadienone

RESULTS

Table 2: Enthalpies of Formation at 298 K.

Species	Δ <sub>f</sub> H <sup>o</sup> <sub>298</sub> kcal mol <sup>-1</sup>	Species	$\Delta_{\rm f} H^{\rm o}_{298}$ kcal mol <sup>-1</sup>	Species	Δ <sub>f</sub> H <sup>0</sup> <sub>298</sub> kcal mol <sup>-1</sup>
y(c <sub>5</sub> h <sub>4</sub> do)	$13.02\pm1.88$	y(c5h3do)oh2-4j	30.46 ± 3.12	y(c5h3do)oh2	$-31.32\pm2.67$
y(c <sub>5</sub> h <sub>3</sub> do)oh2-5j	$34.86\pm3.12$	y(c5h3do)oh3	$-33.52\pm2.67$	y(c5h3do)oh3-2j	$34.15\pm3.12$
y(c <sub>5</sub> h <sub>3</sub> do)q2	$-8.22\pm2.41$	y(c5h3do)oh3-4j	$30.38\pm3.12$	y(c5h3do)q3	$-13.24\pm2.41$
y(c <sub>5</sub> h <sub>3</sub> do)oh3-5j	$31.96\pm3.12$	y(c5h3do)j2	$78.30 \pm 2.22$	y(c5h3do)q2-3j	57.06 ± 2.79
y(c <sub>5</sub> h <sub>3</sub> do)j3	$74.72\pm2.22$	y(c5h3do)q2-4j	57.06 ± 2.79	y(c5h4do)oj2	$-9.36\pm3.06$
y(c <sub>5</sub> h <sub>3</sub> do)q2-5j	$53.98 \pm 2.79$	y(c5h3do)oj3	$\textbf{-6.65} \pm 3.06$	y(c5h3do)q3-2j	57.67 ± 2.79
y(c <sub>5</sub> h <sub>3</sub> do)ooj2	$27.79\pm3.08$	y(c5h3do)q3-4j	$55.40 \pm 2.79$	y(c5h3do)ooj3	$23.98\pm3.08$
y(c <sub>5</sub> h <sub>3</sub> do)q3-5j	$52.04\pm2.79$	y(c5h3do)oh2-3j	$33.88 \pm 3.12$		

Note: j = radical site, y =cyclic ring, d = double bond, q = ooh group

The recommended value in Table 2 for enthalpies of formation at 298 K is calculated via CBS-QB3 level of calculation which is high level calculation and lower uncertainty than B3PLYP/6-31G(d,p) method.



**Figure 1 a and 1b** Chain branching reactions of Cyclopentadienone-2-yl (a), and Cyclo-pentadienone-3-yl radical (b)





**Figure 2**: Rate constants (log k) vs temperature (1000/T) at 50 atm of cyclo-pentadienone-2-yl and Cyclopentadienone-3-yl systems

## Summary

Thermochemical properties were determined by the CBS-QB3 composite calculation method and use of isodesmic work reactions. Thermochemical properties, standard enthalpy of formation ( $\Delta_{\rm f} H^{\rm o}_{298}$ ), entropy heat  $(S^{o}_{298})$ and capacity  $(C_{P}^{o}(T))$ for cyclopentadienone and corresponding 2-hydroxyl cyclopentadienone, 3-hydroxyl cyclopentadienone, 2hydroperoxy cyclopentadienone, and 3- hydroperoxy cyclopentadienone and related radical species are reported. The computed standard enthalpy of formation for the lowest energy conformer of cyclopentadienone from this study is  $13.0 \pm 1.88$  kcal mol<sup>-1</sup> in agreement with data in the literature (13.2 kcal mol<sup>-1</sup>) by Wang and Brezinsky<sup>2</sup> and Burcat and Ruscic<sup>11</sup>, the data is 0.25 kcal mol-1 higher than work of Robinson and Lindstedt<sup>4</sup> (12.75 kcal mol<sup>-1</sup>). The standard enthalpy of

formation for the 2-hydroxyl cyclopentadienone, 3cyclopentadienone, hvdroxvl 2-hydroperoxy hydroperoxy cyclopentadienone, and 3cyclopentadienone are  $-31.3 \pm 2.67$  kcal mol<sup>-1</sup>,  $-33.5 \pm$ 2.67 kcal mol<sup>-1</sup>, -8.2  $\pm$  2.41 kcal mol<sup>-1</sup>, and -13.2  $\pm$  2.41 kcal mol<sup>-1</sup>, respectively. Chain branching reactions, O<sub>2</sub> addition to the 2 and 3 carbon radical sites on cyclopentadienone and further reactions to  $RO \bullet + O$ , intramolecular H atom transfers, and intramolecular peroxy radical additions. The C2 and C3 carbon radical sites on the ring have  $R^{\bullet} + O2 \rightarrow ROO^{\bullet}$ reaction well depths of 50.5 and 50.8 kcal mol<sup>-1</sup>. The Enthalpy of Reaction ( $\Delta H^{0}_{RXN}$ ) for the chain branching reaction to cleave the RO-O bond is only 22.4 and 29 kcal mol<sup>-1</sup> for C2 and C3 peroxy sites respectively as in figure illustrated 1. Reactions involving intramolecular hydrogen transfer reactions have higher barriers, above the RO-O branching reaction and tighter transition state structures; they are calculated to not compete with the branching. The reverse reactions to parent radical + O<sub>2</sub>, which in conventional alkane peroxy radicals, often dominate over the branching reaction, have an endothermicity (barriers) of 50 kcal mol<sup>-1</sup> and will not be too competitive.

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## UNRAVELING THE COMPETING PATHWAYS IN THE REACTION OF HYDROXYL WITH 2-BUTENE.

Leonid Sheps<sup>\*</sup>, Ivan O. Antonov, Justin Kwok,<sup>†</sup> and Judit Zádor Combustion Research Facility, Mail Stop 9055, Sandia National Laboratories, Livermore, CA 94551-0969 USA

We report a detailed experimental and quantum chemical investigation of the pressure- (*P*) and temperature- (*T*) dependent reaction kinetics of OH + 2-butene at engine-relevant conditions: P = 1 - 20 bar and T = 400 - 800 K. Similar to other alkenes, the reaction of OH with 2-butene is characterized by a complex interaction of H abstraction, OH addition to the double bond, and dissociation of the resulting hydroxyalkyl radical adduct (Tully, 1988). This complexity is most apparent in the "intermediate" temperature regime (~ 500 - 700 K in the high-pressure limit), where the rate coefficients of these three pathways are comparable and all three channels compete effectively. With one recent exception of OH + propene (Kappler *et al.*, 2011), there have been no in-depth experimental studies of OH + alkene reactions in the intermediate *T* range, and consequently no direct probing of hydroxyalkyl adduct decomposition.

Using a combination of experimental OH detection (by laser-induced fluorescence) and master equation-based calculations, we present a detailed analysis of the OH + trans- and cis-2-butene reactions over a broad temperature range that includes the challenging "intermediate" *T* region. We employ a sophisticated kinetic analysis scheme that relies on the global interpretation of all experimental data together (i.e. taken at all *T*, *P*, and with both 2-butene isomers as reactants) to produce a self-consistent picture of the OH + 2-butene reaction at *T* < 800 K. As a result, we report parametrized rate coefficient expressions for the relevant kinetic pathways: H abstraction, OH addition, and the dissociation of the 3-hydroxybut-2-yl radical, which is formed by the addition of OH to the double bond of 2-butene. Crucially, 3-hydroxybut-2-yl is a representative of  $\beta$ -hydroxyalkyl radicals, which are key reactive intermediates in the oxidation chemistry of butanols. Our measurement of the decomposition rate coefficient of 3-hydroxybut-2-yl helps fill an important gap in the combustion models of these emerging biofuel candidates.

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<sup>\*</sup> Corresponding author. E-mail: <a href="https://www.lstandia.gov"><u>lstandia.gov</u></a>

<sup>&</sup>lt;sup>†</sup> Current address: Department of Materials Science and Engineering, University of Illinois, Urbana-Champaign

## Computational kinetic study on ROO to QOOH reactions in 2-MTHF oxidation

Prajakta R. Parab<sup>1\*</sup>, Naoki Sakade<sup>2</sup>, Yasuyuki Sakai<sup>2</sup>, Ravi Fernandes<sup>3</sup>, K. Alexander Heufer<sup>1</sup>

<sup>1</sup> Physico Chemical Fundamentals of Combustion, RWTH Aachen University, Templergraben 55, 52056 Aachen,

Germany

<sup>2</sup> University of Fukui, Bunkyo 3-9-1, Fukui, 9108507, Japan

<sup>3</sup> Physikalish Technische Budesanstalt (PTB) Bundesallee 100, 38116 Braunschweig, Germany

#### Abstract

Reaction kinetics of intramolecular hydrogen shift (ROO to QOOH) reactions in 2-methyltetrahydrofuran oxidation is theoretically investigated in this work. These reactions are observed to proceed via formation of cyclic transition states. Computed C-H bond dissociation energy is found to be lowest at the carbon sites neighboring ring oxygen atom. Thermodynamic properties of all the reactants and products species involved in the intramolecular H-shift reactions are presented. Pitzer - Gwinn like approximation has been implemented for the accurate treatment of hindered rotors in reactants, transition states and products. High pressure limiting rate constants for all the isomerization reactions are determined from the three - parameter Arrhenius expression in the temperature range 500-2000 K. All theoretical calculations have been carried out at the CBS-QB3 composite method.

## Keywords

2-Methyltetrahydrofuran, Computational study, Isomerization reactions, High pressure limiting rate constant.

## Introduction

(2-MTHF) 2-Methyltetrahydrofuran is proposed to be a potential fuel component by "Tailor Made Fuels from Biomass (TMFB)" at RWTH Aachen University, Germany based on its combustion behavior, engine efficiency and emission performance [1]. Its synthesis from biomass is also reported via selective conversion of levulinic acid to  $\gamma$ -valerolactone and 1,4-pentanediol [2]. For the development of detailed chemical kinetic model for such fuels, accurate kinetics of highly sensitive reactions must be known for a precise simulation. Kinetic models must also take into an account high as well as low temperature reactions classes in order to cover the wide temperature and pressure regime during simulation. During combustion, formation of alkyl radicals by Habstraction from the fuel by small radical species is of prime importance. Formed alkyl radicals on reaction with O<sub>2</sub> gives rise to peroxy radicals, commonly represented as ROO. In the low temperature regime, further reactions of peroxy radicals gives rise to hydroperoxyalkyl radicals QOOH, via intramolecular H-shift reactions involving formation of cyclic transition state. QOOH radicals can undergo reactions leading to chain branching which ultimately results in autoignition. These low temperature reaction classes play a very important role in predicting Negative Temperature Coefficient (NTC) regime.

Considering furans and its derivatives, very few studies can be found in the literature focusing on the kinetics of its reaction classes. This work highlights detailed computational study on the specific low temperature reaction class in combustion: ROO to QOOH, in 2-MTHF oxidation. These reactions are observed to proceed via formation of cyclic transition states.

## **Computational Details**

Electronic structure calculations involving geometry optimization, vibrational frequencies and single point energy computations of all the reactants, transitions states and products are computed at CBS-QB3 composite method [3, 4]. All electronic structure calculations are performed with the help of Gaussian 09 package [5]. Optimized three dimensional structure of 2-MTHF with the labels used in this study is represented in figure 1.



*Correspondence to:* Prajakta R. Parab Email: parab@pcfc.rwth-aachen.de

# Figure 1. Optimized structure of 2-MTHF at CBS-QB3 method with the labels used in this work.

Considering oxygen position 1, ring carbons are numbered from C2 to C5, while Cm denotes methyl side chain carbon. Hydrogens on the ring are distinguished as cis (c) and trans (t) due to non-planar nature of the ring. Hm represents hydrogens on the methyl side chain (Cm). Vibrational frequencies obtained at B3LYP/CBSB7 level within CBS-QB3 composite method are scaled by 0.99 for zero point energy calculations and by 0.97 for the calculation of the vibrational partition functions. Further, high pressure limiting rate constants are determined for all the ROO to QOOH reaction channels in eight ROO isomers of 2-MTHF. Arrhenius rate parameters for these isomerization reactions are obtained by fitting the calculated rate to the modified Arrhenius rate expression in the temperature range of 500 to 2000 K employing GPOP program [6]. Eckart tunneling corrections [7] are accounted in CTST rate calculation within GPOP. Pitzer - Gwinn like approximations [8, 9] is used for the treatment of low frequency torsional modes in reactants, transition states and products and treated as hindered rotations. Hindered rotor analysis plot for the methyl rotor in 2-MTHF is represented in figure 2. In figure 2a,  $\alpha$  is the dihedral angle, defined between atoms O-C2-Cm-Hm for the methyl rotor in 2-MTHF. Potential energies calculated at CBS-QB3 level for the CH<sub>3</sub> rotor in 2-MTHF is represented by open circles in figure 2b whereas solid line represents Fourier - series interpolation. Eigenstate energies of the hindered rotation are computed using BEx1D program [10]. In figure 2c, open circles indicates partition functions directly derived from eigenstate energies  $(q_{\text{exact}})$  as a function of temperature. Partition function calculated by considering harmonic oscillator approximation is denoted by  $q_{\rm HO}$ , free rotor approximation by  $q_{\rm FR}$  and Pitzer -Gwinn approximation by  $q_{PG}$ . As seen from figure 2c, Pitzer-Gwinn approximation with hindrance potential height of  $V_0 =$ 1050cm<sup>-1</sup> shows an excellent agreement with the exact partition function  $(q_{exact})$ . Hence all the partition functions for CH3 internal rotor in ROO, TS and QOOH are approximated by a Pitzer-Gwinn approximation with hindrance potential height of 1050 cm<sup>-1</sup>. For the CH<sub>3</sub> rotors attached on the carbon centered radical and in transition state involving H2 abstraction, the partition functions were calculated with  $V_0 = 640 \text{ cm}^{-1}$  and  $800 \text{cm}^{-1}$  respectively. Similarly all other internal rotors in reactants, transition states and products are treated as hindered rotors with estimated barrier heights determined by considering Pitzer-Gwinn approximation.

#### Species Abbreviation

Eight ROO isomers are considered as a reactants for the corresponding intramolecular H-shift reactions in 2-MTHF. Cis and trans positions in reactants, transition states and products are

differentiated by alphabet c and t respectively. Alkylperoxy radicals are represented as ROOx wherein x stands for OO position on carbon x. Transition states are abbreviated as TSx-y, in which x is the position of carbon with OO group while the site from which hydrogen atom is abstracted is indicated by alphabet y. QOOHx-y stands for the hydroperoxyalkyl radical (product species) with OOH positioned on carbon x and with radical center y. RCHOx are the product species formed as a result of 1,3 H-shift reaction channels.



Figure 2. Hindered rotor analysis for the methyl rotor attached to the C2 atom in the tetrahydrofuran ring; (a) definition of torsional angle a, for methyl rotor (b) potential energy calculated by using a CBS-QB3 method (open circle) and fitted curve (line) (c) Partition function calculated from eigenstate energies ( $q_{exact}$ ) in comparison with harmonic oscillator ( $q_{HO}$ ), free rotor ( $q_{FR}$ ) and Pitzer–Gwinn ( $q_{PG}$ ) approximations.

## **Results and Discussion**

#### **Bond Dissociation Energies**

C-H Bond Dissociation Energies (BDEs) for all bonds in 2-MTHF are computed at CBS-QB3 composite method and summarized in Table 1. C2-H and C5-H bonds with BDE values of 382 kJ mol<sup>-1</sup> and 386 kJ mol<sup>-1</sup> respectively are observed to be the weakest C-H bonds in 2-MTHF. Lower BDEs at these sites in 2-MTHF is due to the presence of electronegative oxygen atom neighboring C2 and C5 which ultimately tends to affect its C-H bond strengths. Observed trend in C-H BDEs in 2-MTHF is as follows: C2-H2 < C5-H5 < C4-H4 < C3-H3 < Cm-Hm. As seen from table 1, BDE at C5 is 23 and 18 kJ mol<sup>-1</sup> lower than at C3 and C4 sites respectively. As expected, highest BDE value of 424 kJ mol<sup>-1</sup> is observed for the Cm-Hm bond which corresponds to the primary C-H bond in 2-MTHF.

*Table 1.* C-H bond dissociation energies in 2-Methyltetrahydrofuran

bond <sup>a</sup>	$D_0$ <sup>b</sup> / kJ mol <sup>-1</sup>
C2-H2	382
C3-H3t or C3-H3c	409
C4-H4t or C4-H4c	404
C5-H5t or C5-H5c	386
Cm–Hm	424

<sup>*a*</sup> Atom labels are given in the figure 1. <sup>*b*</sup> C-H bond dissociation energies calculated at CBS-QB3 level.

### Thermochemistry

Thermodynamic properties (standard enthalpies of formation, standard entropies and heat capacities at constant pressure) for all the reactants involved in the isomerization reactions of 2-MTHF are computed by using atomization method employing CBS-QB3 composite method and summarized in table 2. Experimental data on thermodynamic properties of 2-MTHF and its derivatives are not available in the literature. Hence, standard enthalpy of formation  $(\Delta_{\rm f} H^{0}_{298})$ and standard entropy  $(S^{0}_{298})$ for terahydrofuran and its radical species are computed at CBS-QB3 level and compared with experimental data from the literature. Due to the reasonable agreement observed between the theoretical and experimental results, this method is adopted for computing thermodynamic properties of all the species involved in this study.

Table 2. Standard enthalpies of formation  $(\Delta_f H^0_{298})$  and standard entropies  $(S^0_{298})$  at 298.15 K, and heat capacity at constant pressure  $(C_p)$  for temperatures between 300 and 1500 K for ROO isomers in 2-MTHF.

Secondae		Δ <sub>t</sub> H <sub>291</sub> (k.mo) (.r	S 293	$C_{\rm p}(J{ m mol}^{-1}{ m K}^{-1})$						
opeores	(. mo X - )		300 K.	400 K.	500X	600 X.	800 K	1000 K	1500 K	
	R002	-213.91	391.45	139.48	177.47	209.63	235.74	274.77	302.41	343.75
	ROO3c	-170.89	395.89	137.00	174.98	207.58	234.15	273.91	301.99	343.72
	R003t	-175.95	397.83	136.78	74.97	207.65	234.26	274.01	302.07	343.76
	R004c	-176.40	396.11	136.39	74.68	207.44	234.12	273.98	302.10	343.84
	R004:	-176.79	392.73	136.92	175.04	207.69	234.28	274.05	302.13	343.83
	ROOSe	-205.23	393.61	137.04	175.39	208.04	234.55	274.13	302.08	343.68
	ROOSI	-201.41	391.96	136.93	175.13	207.75	234.28	273.93	301 <b>.9</b> 4	343.62
	ROOm	-156.31	401.15	130.54	170.70	205.82	234.44	276.64	305.77	348.14

Table 3. Reaction barriers, energies and rate constants for the hydrogen shift reactions in 2-MTHF

un entrant (		TT -4 h	E0°	$\Delta E^{d}$	rate	constan	t <sup>e</sup>
Teactain	product	11 410111	kJ mol-1	kJ mol-1	А	п	E/R
ROO2	QOOH2-3	H3c	222	51	4.45E+03	2.511	13199
	00011-4	H3C H4t	155	51 47	2 022-04	2.064	11/105
	QOOI12-4	LISI	61	22	7.390±04	1 664	2230
	Q00112-J	Lim	1.40	70	1.200100	1.004	14704
<b>P</b> O024	000H2-11	110	195	14	0.550-02	2.009	10122
ROOM	DCHO3TOR	H3t	170	174	6 600102	2.323	19144
	KCHO5+OH	HAO	136	42	0.0015105	2.134	10457
	QOOH3c-4	H4t	202	53	1.07E+02	2.928	12982
	QOOH3e-5	H5c	93	33	2.30E+05	1.749	9198
	QOOII3c-m	Hm	97	68	2.28E105	1.845	9874
ROO3t	QOOH3t-2	H2	100	19	2.82E+05	1.872	9980
	RCHO3+OH	H3c	171	-119	4.10E+05	2.123	18593
	0001221	H4c	204	56	7.4872400	3 744	14319
	QUU1314	H4t	144	56	7.4JETUZ	2./44	14210
	QOOH3t-5	H5t	96	35	1.27E+05	1.820	9524
	QOOH3t-m	Hm	127	68	1.80E+04	2.137	13001
RO04c	000H4c-3	H3c	136	56	2 98E+02	2 810	13234
ROUTE	QUUINE 5	H3t	206	56	1.501.101	2.012	15254
	RCH04+OH	H4t	175	-120	5.68E+05	2.137	19164
	OOOH4c-5	H5c	110	28	5.15E+04	2.080	10897
	·	H5t	193	28	2.000.004	2 0 2 1	
<b>BOO</b> 44	QUUH4c-m		114	70	2.00E+04	2.031	11495
ROU4t	QOOH40-2	ПZ Ц2о	200	51	1.32E+00	1.029	6/33
	QOOH41-3	Hat	209	60	1.99E+03	2.688	14263
	рснои∔он	H4c	173	-119	6 228405	2 164	18843
	101104+011	HSc	197	23	0.221.103	2.105	10055
	QOOH41-5	H5t	107	23	6.35E+04	2.116	10531
RO05c	QOOH5c-3	H3c	116	44	3.13E+04	2.076	11810
	-	H4c	138	48	e tatuloa	2 602	12022
	QUUH5C-4	H4t	218	48	7.14E+03	2.503	13925
	RCHO5+OH	H5t	169	-171	8.53E+06	1.778	18767
	QOOH5c-m	Hm	124	60	5.35E+03	2.249	12650
RO05t	QOOH5t-2	H2	75	24	3.08E+06	1.534	7361
	QOOH5t-3	H3t	114	40	4.16E+04	2.080	11432
	00000444-4	H4c	213	41	2 147-403	2 630	12882
	Acount.	H4t	131	41		2.000	12002
	RCHO5+OH	H5c	163	-175	5.88E+06	1.778	18046
ROOm	QOOHm-2	H2	104	23	4.69E+05	1.765	10442
	QOOHm-3	H3c	78	46	3.33E+06	1.387	7969
		H3t TT4-	146	46	1.8172105		
	QOOHm-4	H40	80	4 <i>5</i> 10	3.71E+05	1.562	86 <i>33</i>
	QUUHm-5	HJC	52 1.60	∠6 10#	7.79E+05	1.453	5148
	RCHOm+OH	. Hm	109	-105	1.71E+06	1.938	18466

<sup>*a*</sup> Reactants and products abbreviations, <sup>*b*</sup> The position of hydrogen atom being abstracted as given in the figure1, <sup>*c*</sup> Reaction barrier. <sup>*d*</sup> Reaction energies. <sup>*e*</sup> Rate constants are given by the Arrhenius expression,  $k / s^{-1} = AT^{n} \exp(-E/RT)$ .

#### **Reaction Barriers and Energies**

Reaction barriers  $(E_0)$  and energies  $(\Delta E)$  for the titled reactions in 2-MTHF are computed at CBS-QB3 composite method and summarized in table 3. In all ROO isomers, 1,5 H-shift is observed to be the most favorable reaction channel accompanied with lowest

reaction barrier except in the case of ROO4c in which 1,4 H-shift is predominant. It is due to the fact that in ROO4c isomerization reaction via formation of six membered transition state is infeasible due to the trans position of abstracted hydrogen to the peroxy group.

#### High Pressure Limiting Rate Constants

High pressure limiting rate constants are determined for all possible intramolecular H-shift reaction channels in ROO isomers of 2-MTHF and summarized in table 3. Rate constants are determined by fitting the calculated rate to the modified Arrhenius rate expression,  $k = AT^{n}\exp(-E_{a}/RT)$  in the temperature range of 500 to 2000 K. Arrhenius plot representing H-shift reaction channels in ROO2 isomer of 2-MTHF are summarized in figure 3.



Figure 3. High pressure limiting rate constants for the intramolecular hydrogen shift reactions in ROO2 isomer of 2-MTHF.

As seen from figure 3, faster rate constant is observed for QOOH2-5 formation which involves hydrogen abstraction from C5 site, neighboring ring oxygen atom. This result is found to be consistent with the computed C5-H BDE which is lowest than C3-H, C4-H and Cm-H BDEs attributing to the most favorable Hshift channel. Formation of QOOH2-4 and QOOH2-3 proceeds via six and five membered transition state ring respectively wherein former channel is more feasible as comprehended by its reaction kinetics. The slowest rate constant is depicted for the H-shift from methyl side chain leading to the formation of QOOH2m. Cm-H bond as discussed before in BDE section, is the primary C-H bond in 2-MTHF with its BDE value of 424 kJ mol<sup>-1</sup>.

## Conclusion

This work highlights detailed theoretical study on one of the important low temperature reaction class: ROO to QOOH in 2-MTHF oxidation. These reactions involves intramolecular H-shift taking place via formation of cyclic transition state. Strength of the C-H bond is the main factor affecting the kinetics of these isomerization reactions. Lowest C-H BDEs are found to be at C2 and C5 sites (382 and 386 kJ mol<sup>-1</sup>) respectively) while Cm-H (424 kJ mol<sup>-1</sup>) depicts highest BDEs among all the C-H bonds in 2-MTHF. Isomerization reactions proceeding via five and six membered transition state ring are highly favorable and associated with the lowest reaction barriers.

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## Kinetic Isotope Effect of C<sub>2</sub>H<sub>6</sub> + OH and C<sub>2</sub>D<sub>6</sub> + OH: Experimental and Theoretical Study

Fethi Khaled<sup>1</sup>, Binod Raj Giri<sup>\*1</sup>, Milán Szőri<sup>2</sup>, Béla Viskolcz<sup>2</sup> and Aamir Farooq<sup>\*1</sup>

<sup>1</sup> Clean Combustion Research Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Saudi Arabia

<sup>2</sup>Department of Chemical Informatics, Faculty of Education, University of Szeged, Boldogasszony sgt. 6 H-6725

Szeged, Hungary

\*Corresponding author: <u>aamir.farooq@kaust.edu.sa</u>

### Abstract

We report experimental and theoretical results for the kinetic isotope effect of the reaction of OH with ethane (C<sub>2</sub>H<sub>6</sub>) and deuterated ethane (C<sub>2</sub>D<sub>6</sub>). The two reactions, C<sub>2</sub>H<sub>6</sub> + OH and C<sub>2</sub>D<sub>6</sub> + OH, were investigated separately behind reflected shock waves over 800 – 1300 K and pressures near 1.5 atm. Reaction progress was followed by monitoring OH radicals near 306.69 nm using laser absorption technique. Hydroxyl radicals were produced by rapid thermal decomposition of tert-butyl hydroperoxide (TBHP). The best fit of the experimental data of the two reactions yields the following modified Arrhenius expression for the deuterated kinetic isotope effect (DKIE):  $\frac{k_{C2H6+OH}}{k_{C2D6+OH}} = 0.1866 \cdot T^{0.2173} \cdot \exp(\frac{616K}{T})$ . Experimental results show that the ethane DKIE at high temperatures aysmptotes to 1.4 which is consistent with the results obtained using high level quantum chemical and statistical rate theory calculations.

## Keywords

Ethane, Deuterated Ethane, Hydroxyl Radicals, Quantum Chemical Calculations, Isotopic Effect, Statistical Rate Theory.

### Introduction

Small alkanes (< C5) constitute almost all of the composition of natural and liquefied petroleum gas (LPG), whereas larger straight or branched alkanes  $(\geq C5)$  are the primary constituents of gasoline, diesel and aviation fuels. Hydrogen abstraction reactions from alkanes by hydroxyl radicals (OH + RH  $\rightarrow$  R + H<sub>2</sub>O) are the primary oxidation pathways of these fuels at combustion conditions. Accurate modeling of combustion kinetics requires precise knowledge of total and site-specific rate coefficients over a wide range of temperatures and pressures. A conventional way to derive overall and site-specific rate coefficients is to start from small chain fuels and then use group additivity approximations to estimate rate coefficients for longer chain species. Various approximations have been used in literature such as the next-nearestneighbor (NNN) (Cohen 1982)<sup>,</sup> (Sivaramakrishnan and Michael 2009) or structure activity relationship (SAR) (Kwok and Atkinson 1995). Tully and co-workers pioneered the use of deuterium kinetic isotope effect (DKIE) to extract rules for the calculation of sitespecific rates of H-abstraction from a variety of molecules. This methodology has, for example, been used to discern the branching ratios of the three competing channels during the reaction of propane with OH at low temperatures (Droege and Tully 1986) and high temperatures (Badra et al. 2014b). Recently, (Badra et al. 2015) published detailed analysis and experimental results on the application of DKIE to

extract branching ratios of the three competing channels during the reaction of propene with OH radicals at high temperatures. The importance of DKIE of small molecules such as ethane, ethylene and acetylene in the determination of branching ratios of longer chain alkanes, alkenes and alkynes is demonstrated therein (Badra et al. 2015). The aim of this work is to extend low temperature (290-800 K) data on DKIE of ethane (Tully et al. 1986) to high temperatures (800-1300 K) using rate coefficients measurements of the reaction of ethane and deuterated ethane with OH:

$$C_2H_6 + OH \rightarrow C_2H_5 + H_2O \tag{R1}$$
  

$$C_2D_6 + OH \rightarrow C_2D_5 + HDO \tag{R2}$$

These results will be helpful in elucidating the competition of the different H-abstraction channels during the reaction of larger alkanes with OH radicals.

#### **Experimental Setup**

The low pressure shock tube facility (LPST) at King Abdullah University of Science and Technology (KAUST) was used to conduct all the experiments presented here. Detailed description of this facility can be found in (Badra et al. 2014a). In nutshell, the LPST has 9 m long driver and driven section. The driver section length can be modified to 6 m or 3 m depending on the required test time. Optical windows are installed at a sidewall location, 10 mm from the endwall of the shock tube. Hydroxyl radicals are measured by using the well-characterized R1(5) absorption line in the (0,0) band of the A<sup>2</sup>  $\Sigma^+ \leftarrow X^2 \Pi$ transition of OH radical near 306.7 nm. Measured absorbance signal is converted to OH concentration using the Beer-Lambert law. Hydroxyl radicals are produced by rapid thermal decomposition of tert-butyl hydroperoxide (TBHP), which is known to be a clean OH precursor and has been validated in many studies (Vasudevan et al. 2005). A 70% TBHP in water solution was obtained from Sigma Aldrich. Ethane (99.99%), argon (99.999%), and helium (99.999%) were purchased from AH Gases. Ethane-d<sub>6</sub> (98%) is obtained from CDN Isotopes Inc. Several reflectedshock experiments were conducted for each fuel (C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>D<sub>6</sub>) and the concentrations of reactants (fuel, TBHP) were chosen based on sensitivity analysis while maintaining pseudo-first-order conditions.

## **Computational Details**

The molecular and transition geometries were optimized at the MP2/cc-pVTZ level of theory (Dunning 1989); (Hehre et al. 1986); (Moller and Plesset 1934); applying the 'tight' convergence criterion of the Gaussian09 program package. The MP2/cc-pVTZ harmonic vibrational wavenumbers of the molecules and transition states were scaled by a factor of 0.95 adopted from CCCBDB database. Similar to previous works (Bansch et al. 2013; Farago et al. 2015; Izsak et al. 2009), the accurate description of the electronic structures was approximated by extrapolation schemes. While Feller extrapolation (Feller 1992) was utilized for HF energies (using ccpVXZ basis sets, where X=D, T and Q) (Dunning 1989) Helgaker extrapolation for CCSD(T) correlation energies (Watts et al. 1993) was applied (Helgaker et al. 1997) with cc-pVTZ and cc-pVQZ basis sets. Sum of these extrapolated energies manifested in CCSD(T)/cc-pV(T,Q)Z//MP2/cc-pVTZ level of theory which is chosen to establish high-level ab initio description of the zero-point corrected relative energies  $(\Delta E_0)$  for both isotopologues.

The rate constants of ethane + OH and ethaned<sub>6</sub> + OH can be described by canonical transition state theory (CTST) with molecular and transitions state data from our *ab initio* calculations. In these CTST calculations, all species were assumed to be in the electronic ground state except OH, for which the electronic partition function was calculated with a spin orbit splitting of 139.7 cm<sup>-1</sup> (Herzberg 1989).

## Ethane (H/D) + OH Rate Coefficients

The JetSurf 1.0 mechanism has been selected to model the OH mole fraction time evolution. Tertbutyl hydroperoxide (TBHP) sub-mechanism was added to model the TBHP decomposition behind reflected shock waves. Sensitivity analysis was performed to explore the primary reactions that affect OH concentration profile in our experimental conditions (see *Figure 1*). Measurements of R1 were carried out in the temperature range of (847-1285 K) using a mixture of 342 ppm of ethane with TBHP diluted in argon. Measurements of R2 ranged from 805 to 1345 K using a mixture of 310 ppm of ethane- $d_6$  with TBHP diluted in argon. The concentration of TBHP is guaranteed to be less than  $1/10^{th}$  of that of ethane and ethane- $d_6$  to follow pseudo-first order kinetics.



Figure 1: Hydroxyl sensitivity for a mixture of 342 ppm ethane with 22.4 TBHP and 70 ppm water diluted in argon at 1106 K and 1.38 atm

The rate coefficients of reactions R1 and R2 are calculated by fitting the simulated [OH] to the experimental [OH] decay. Repersentative experimental and modeled OH profiles for ethane and ethane- $d_6$  are presented in *Figure 2* and *Figure 3*, respectively.



Figure 2: Hydroxyl mole fraction profile for ethane + OH reaction



Figure 3: Hydroxyl mole fraction profile for ethane-d6 + OH reaction

Measured rate coefficients are grouped in *Table 1* and *Table 2* and plotted in *Figure 4* together with previous low temperature data from (Tully et al. 1986).

Temperature (K)	Pressure (atm)	$k_1(\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1})$
847	1.68	4.10E+12
925	1.6	5.38E+12
970	1.46	6.40E+12
1034	1.4	7.39E+12
1106	1.38	8.40E+12
1142	1.31	9.26E+12
1275	1.31	11.7E+12
1277	1.08	12.5E+12
1285	1.21	11.8E+12

Table 1:Measured Rate coefficient of reaction R1

 Table 2: Measured rate coefficient of reaction R2

Temperature	Pressure	$k_2(cm^3 \cdot mol^{-1} \cdot s^{-1})$
(K)	(atm)	
805	1.68	1.86E+12
875	1.63	2.69E+12
943	1.56	3.45E+12
997	1.34	4.46E+12
1030	1.62	4.97E+12
1133	1.44	6.02E+12
1190	1.44	6.87E+12
1240	1.28	7.84E+12
1254	1.42	7.97E+12
1345	1.37	9.61E+12

## Deuterated Kinetic Isotope Effect of Ethane (H/D)

Our calculated energy profile of the reaction of ethane isotopologues with OH is shown in Figure 5. The *ab initio* reaction energy for ethane (-75.9 kJmol<sup>-1</sup>) agrees within the uncertainty (1.70 kJmol<sup>-1</sup>) of the experimental value (-76.01 kJmol<sup>-1</sup>) calculated from data available in the CCBDB database. Our ab initio barrier (9.3 kJmol<sup>-1</sup>) height is also found to be consistent with Ref. (Melissas and Truhlar 1994). These results allow us to assume that energies calculated here for the deuterated species are also highly accurate. Therefore, from the results of ab initio calculations, we calculated DKIE as the ratio of rate coefficients of reactions R1 and R2, using CTST. Both experimental and calculated DKIE results are displayed in Figure 6. The best fit of experimental data (this work and Tully et al. 1986) on the DKIE yields the following modified Arrhenius expression (293 K -1300 K):

$$\frac{k_{C2H6+OH}}{k_{C2D6+OH}} = 0.1866 \cdot T^{0.2173} \cdot \exp(\frac{616K}{T}).$$

The comparison of the calculated and experimental DKIE values shows good agreement over the entire temperature range, even if the CTST gives a factor of 1.81 faster rate constants than the corresponding measurements for both R1 and R2. This is likely due to the missing hindered rotor treatment.



Figure 4: Rate coefficients of the reaction of ethane and ethane-d<sub>6</sub> with OH: circles (this work), triangles (Tully et al. 1986)



Figure 5: Zero-point corrected energy profiles of the H-abstraction from ethane isotopologues



Figure 6: Comparison of the experimental and theoretical DKIE of ethane (H/D) +OH

#### Conclusions

The deuterated kinetic isotope effect (DKIE) of the reaction of ethane and ethane- $d_6$  with OH radicals has been investigated experimentally between 800 and 1300 K. The obtained high temperature DKIE values together with low temperature results by Tully *et al.* are consistent with the calculated DKIE for the entire temperature range (300-1300 K).

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# EXPERIMENTAL DESIGN IN NON LINEAR CASE APPLIED TO HYDROCRACKING MODEL: HOW MANY POINTS DO WE NEED AND WHICH ONES?

Benoit Celse\*, JJ. Da Costa and V. Costa IFPEN, Lyon Establishment – Rond Point de l'Echangeur de Solaize BP 3 – 69360 Solaize - France

#### Abstract

In this work, different experimental design techniques were applied to a hydrocracking conversion model (single-response). The selection of points was carried out using Federov's algorithm from an experimental database containing 48 points. 3 different criteria were explored: D-, I- and A-optimality. The sequential design methodology was also applied. Results show that the D-optimality criterion is adequate for the determination of the minimum number of experiments required to achieve acceptable precision. It is shown that only 22 points are enough to estimate parameters instead of the original database of 48 points. If sequential techniques are used, only 13 points are needed. This work provides useful theoretical and practical guidelines for experimental design in single-response problems.

## Keywords

Design of experiments, D optimality, non linear model, Hydrocracking

#### Introduction

Upgrading of heavier crude oil residues to more valuable light and middle distillates is becoming increasingly important for the global refining industry because of the decline in conventional, light crude oil sources [1], combined with the increasing demand for fuel oil and middle distillates due to the rapid growth of developing countries such as China or India. Hydroconversion, which accounts for 15 - 17 % of global residue processing capacity [2], is an extremely versatile process, capable of treating a wide variety of feedstocks, including light and heavy crude, vacuum gas oil (VGO), bitumen, as well as other nonconventional resources such as shale oil or vegetable oils. Hydroconversion of VGO is performed by hydrotreatment (HDT) and hydrocracking (HCK) in two reactors in series. The HDT step is mainly concerned with the removal of impurities; notably the elimination of sulfur and nitrogen from the organic hydrodearomatization components via (HDA, hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions. The majority of the cracking and thus production of lighter and more valuable fractions occurs in the subsequent HCK reactor.

Kinetic reactor models are a crucial tool in the design, process optimization and operation of commercial HCK reactors. Chemical engineers not only need to be able to estimate the performance of a new reactor design, but also require accurate predictions in order to choose the optimal operating conditions of an existing unit after a change in feedstock and/or catalyst. Models are a combination of the structure of the model itself (i.e. kinetic rate expressions, reaction framework) with a set of empirically determined parameters. Ideally, the model should be as robust as possible and be applicable over a wide range of operating conditions and feedstock characteristics in order to be useful to the chemical engineers. The structure of the model can be determined from first principles and empirical engineering considerations. Typically, it is desired to establish the most appropriate model structure and the best values of the parameters, so as to provide the best fit to the experimental data [3].

Despite the importance of this problem, there has been relatively little work in the past on the application of experiment design techniques. The aim of this paper is to illustrate these techniques on a simple hydrocracking example. It is structured as follows:

- First section details theoretical background;
- Second section gives an application example.

#### **Theoretical description**

## Experimental Design

An important branch of statistics is the theory of optimal experimental designs, which explains how to best select experiments in order to estimate a vector of parameters  $\theta$ . The reader is referred to the monographs of Fedorov [4] for a comprehensive review on the subject, and to articles of Atkinson [5] for more details on the early development of this theory. The aim of experiment design for improved parameter precision is to decrease the size of the inference regions of each of the parameters in any given model [3]. This is equivalent to making the elements of the parameter variance-covariance "small". Thus, one may start with an estimate of the highest posterior density (HPD) region, and, in particular, the marginal posterior density covariance as given by [6]:

$$V(\hat{\theta}, \varphi) = \left[\sum_{r=1}^{M} \sum_{s=1}^{M} \sigma_{r,s} S_r^t S_s + \left(\sum_{\theta} (\hat{\theta})\right)^{-1}\right]^{-1} (1)$$
  
With :

- φ: vector of experiment decision variables to be determined by experimental design;
- S<sub>r</sub>: matrix of partial derivatives of the r<sup>th</sup> response in the model with respect to the parameters θ calculated at the n experimental points. Each line of the matrix S<sub>r</sub> corresponds to one experimental point;
- σ<sub>r,s</sub>: rs<sup>th</sup> element of the inverse of the estimate Σ of the variance-covariance matrix of the residuals estimated by :

$$\sigma_{r,s} = \frac{\sum_{i=1}^{N} \left[ \left( y_{ri} - \widehat{y_{ri}(\hat{\theta})} \right) \left( y_{si} - \widehat{y_{si}(\hat{\theta})} \right) \right]}{N-1}$$
(2)

•  $\sum_{\theta}(\hat{\theta})$  is an approximate variance-covariance matrix of the parameters.

As suggested by Box and Lucas [7], prior information on  $\hat{\theta}$  is ignored by dropping the dependency on  $\sum_{\theta}(\hat{\theta})$ . Thus the design of experiments to improve parameter precision reduces to minimizing some metric of:

 $V(\hat{\theta}, \varphi) = \left[\sum_{r=1}^{M} \sum_{s=1}^{M} \sigma_{r,s} S_{r}^{t} S_{s}\right]^{-1} (3)$ 

The same demonstration can also be read in Draper and Hunter [8]. Therefore, an information matrix for experiment design can be defined for the improvement of parameter precision in non-linear and multi-response systems. The design criterion requires maximizing a metric of the information matrix, defined in the following way

$$M(\hat{\theta}, \varphi) = \left[\sum_{r=1}^{M} \sum_{s=1}^{M} \sigma_{r,s} S_r^t S_s\right]^{-1}$$
(4)  
In order to compare the magnitude of di

In order to compare the magnitude of different matrices, various real-valued functions have been suggested as metrics. Three common criteria are:

1. D-optimality: an experimental design is Doptimal if it minimizes the determinant of the covariance matrix (3), and thus minimizes the volume of the joint confidence region. This criterion is invariant under linear transformations of the parameter vector, which frees them from a dependency on units of scale;

2. E-optimality: an experimental design is Eoptimal if is minimizes the largest eigenvalue of the covariance matrix (3), and thus minimizes the size of the major axis of the joint confidence region;

3. A-optimality: an experimental design is Aoptimal if it minimizes the trace of the covariance matrix (3), and thus minimizes the dimensions of the enclosing box around the joint confidence region.

## Sequential Design

A class of attractive alternatives to local optimality is given by sequential designs. The asymptotic theory related to this is most well developed for the case of D-optimality. Here it is

supposed that one will obtain n1 observations from an initial, static design. These are used to give initial estimates of the parameters, following which the remaining n - n1 observations are made sequentially, at each stage choosing the next design point so as to maximize the determinant of the information matrix evaluated at the current parameter estimates. Chaudhuri and Mykland [9]show that, under certain conditions, the obtained sequence of designs converges to the Doptimal design for the true parameters. These conditions include the requirement that  $n1/n \rightarrow 0$  as both n and n1 tend to infinity and an assumption that the parameter estimates be consistent. A consequence is that inferences made from a sequentially constructed design have the same asymptotic properties as if they were made following a static design — an observation previously made by Wu [10] in a related context. Sinha and Wiens [11] extend the ideas of Chaudhuri and Mykland, and incorporate some uncertainty as to the nature of the parametric model. Dror and Steinberg [12] introduce significant improvements to these methods; in particular their sequential procedure for design construction is easily adapted to multifactor experiments and to a range of possible models.

## Application

Data

The experimental runs presented in this study were performed in a pilot unit at IFP Energies Nouvelles, Solaize, France. The hydrocracking step was performed on a commercial catalyst. Various commercial HDT catalysts were used for the pretreatment step. The plant consists of a number of fixed beds, downflow reactors, designed to mirror the operating conditions in industrial hydrocracking units. Unlike industrial units, which operate in adiabatic mode, the pilot plant operates in isothermal conditions. The experimental runs were carried-out in continuous operation. Individual mass balances were taken for up to 12 hours, after temperatures, pressures, flow rates, and effluent properties were stabilized. A series of mass balances with different operating conditions were thus taken from each experimental run. Each mass balance corresponds to a single experimental point. Analyses were performed on the feedstocks, the liquid and gaseous effluents.

#### Model

The previous theory is applied to a simple model on R2 conversion. Some more complex models exist but for simplicity it is preferable to focus on simple example results [13]:

$$\frac{dy}{dt} = \frac{k_0}{(1+\beta N_{R2}^{\alpha})} \left(\frac{H2/HC}{N_{R1}P_{tot}}\right)^b TMP^c \exp\left(\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) \quad (4)$$

Where:

- T: temperature (°C);
- NR1: nitrogen content in the feed of R1 (wppm);
- Ptot: Total pressure (bar);

- NR2: nitrogen content of the liquid stream entering into R2 (wppm);
- y: conversion of the 370°C+ fraction (%);
- t: contact time (h);

The model parameters are:  $k_0$  (pre-exponential factor), Ea (activation energy) and  $\alpha$ , b, c.

This model has been calibrated using 48 experimental runs in a pilot plant, with different feeds. Feed characteristics (SIMDIS, sulfur/nitrogen content, aromatic carbon content etc.) for the feed of the second reactor were known. Temperature was varied from 360 to 400°C, and liquid hourly space velocities (LHSV), which corresponds to the inverse of contact time, varied from 1.0 to 3.5 h-1. Experiments were performed at 100 and 140 bar, with an ammoniac partial pressure (ppNH3) within 0.1 to 1.5 bar and a hydrogen to oil ratio (H2/HC) of 600 to 1400 StdL/L. The following figure (cf. *Figure 1*) shows the obtained results with the 48 points. The model is precise.



Figure 1. Obtained parity plot.

## Application

The aim of this study is to apply experimental design theory in order to choose the best set of points among the 48 candidates. The initial parameters used are obtained using the previous generation of the catalyst. The AlgDesign package on R has been used [14]. This package calculates exact and approximate theory experimental designs for D, A, and I criteria. Approximate designs weight the candidate points with a probability measure, which for practical purposes amounts to allowing unequal replication.

The Federov algorithm [4] starts with n points chosen in  $\varphi$  (set of possible experimental points). They may be chosen randomly or by expert design. It exchanges points in the n point design Z with points in  $\varphi$ -Z, i.e. points not in Z, in order to optimize a criterion. It quits when no profitable exchanges are possible, or the input parameter maxIteration is reached. The quality of the result depends on the starting design and the result may represent a local optimum. The procedure is repeated n times in order to approach the global optimum.. The information matrix defined previously (see equation (4)) is then chosen.

The following indicators are chosen to compare the different set of parameters:

• The mean absolute deviation of the 370+ cut:

$$\Delta C_{370+} = \frac{1}{n} \sum_{i=1}^{n} |C_i^{simule} - C_i^{experimental}|$$

• The percentage of points at different levels of precision:

$$\tau_{\pm 2\%} = \frac{\sum_{i=1}^{n} 1_{|C_i^{simule} - C_i^{experimental}| \le \tau}}{n}$$

Where  $\tau$  stands for 2%, 5%, 10%.

• The mean absolute value in temperature:

$$\Delta T_{moyen} = \frac{1}{n} \sum_{i=1}^{n} |T_i^{après\ opt} - T_i^{expérimental}|$$

 $T_i^{après opt}$  are obtained by fixing all the other variables in the model around a given set of parameters and to calculate the temperature required in order to obtain the experimental conversion.

• The percentage of points at different levels of precision in temperature (with t=2, 3, 5):

$$\tau_{\pm t^{\circ}C} = \frac{1}{n} \sum_{i=1}^{\infty} \mathbf{1}_{|T_{i}^{après \, opt} - T_{i}^{expérimentale}| \le t^{\circ}C}$$

• The sum of residuals:

$$SCR(\theta) = \sum_{i=1}^{n} (C_{i}^{simul\acute{e}} - C_{i}^{exp\acute{e}rimental})^{2}$$

The first problem to solve is to choose the right number of points in order to fit the model. We suggest to study the evolution of the D-optimal criteria. Some trials show that an efficiency (i.e. D-optimal criteria at n points divided by the D-optimal criteria with 48 points) at about 0.9 is enough. For example, in our case (Figure 2), it is shown that about 30 experimental points are enough to estimate the parameters accurately. We test other criteria (D and I) but no differences have been seen.

Table 1 contains the indicators obtained with the calibration database (22 points) and with global database (48 points). The following results can be deduced: 1/ Both models provide the same range of quality indicators. 2/ These indicators are good, which means that the model with 22 points has a similar precision to the one with 48 points.

The sequential design method has been applied to the global database with two iterations. The first iteration is carried out with 10 experimental points and the second iteration with 3 experimental points. Table 2 compares the obtained results. The experimental set with 13 points leads to similar precisions when compared to the set containing 48 points.

## Conclusion

This work shows that experimental design can be used to reduce drastically the number of experimental points needed to estimate model parameters. In our case, 22 points are enough to estimate parameters when compared to the original database of 48 points. The sequential design method can also be used. In our case it is very efficient. Some improvements are still required to extend the proposed methodology to several responses. However, it should be straight forward due to the fact that the theory is well established.



Figure 2. D-optimal criteria.

Table 1. Experimental design results						
Indicators	22 points	48 points (Ref)				
$\Delta C_{370+}$	2.63	2.61				
$ au_{\pm 2\%}$	56.25	41.66				
$ au_{\pm 5\%}$	85.41	87.50				
$ au_{\pm 10\%}$	100.00	100.00				
$\Delta T_{moyen}$	1.49	1.45				
$ au_{\pm 2^\circ \mathcal{C}}$	75.00	77.08				
$ au_{\pm 3^\circ \mathcal{C}}$	89.58	87.50				
$ au_{\pm 5^\circ \mathcal{C}}$	93.75	100.00				
SCR	625.00	530.00				

Table 2 Sequential Design Results						
Indicators	Sequential	48 points (Ref)				
$\Delta C_{370+}$	2.77	2.61				
$ au_{\pm 2\%}$	50.00	41.66				
$ au_{\pm 5\%}$	85.41	87.50				
$ au_{\pm 10\%}$	100.00	100.00				
$ au_{\pm5\%}$	1.45	1.45				
$ au_{\pm 2^\circ \mathcal{C}}$	77.08	77.08				
$ au_{\pm 3^{\circ}\mathcal{C}}$	87.50	87.50				
$ au_{\pm 5^{\circ} C}$	100.00	100.00				
SCR	698.00	530.00				

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# Reactor Optimization for Maximized Propene Yields in Olefins Cracking on ZSM-5 using Single-Event Methodology

Tassilo von Aretin\* and Olaf Hinrichsen Technische Universität München, Department of Chemistry, Lichtenbergstraße 4, 85748 Garching b. München, Germany Technische Universität München, Catalysis Research Center, Ernst-Otto-Fischer-Straße 1, 85748 Garching b. München, Germany

Reactor Optimization, Olefins Cracking, Single Events, ZSM-5

The complex reactivity of olefins on ZSM-5 can be described with the single-event methodology<sup>1,2</sup>. In this work a single-event kinetic model for the catalytic cracking of 1-pentene<sup>3</sup> on ZSM-5 is used to optimize a reactor for olefins cracking in terms of propene yield. Kinetic parameters to describe the reactivity of 1-pentene are estimated from a large data set with 23 experimental conditions being varied in 165 different experiments<sup>3</sup>.

With this single-event kinetic model the reaction temperature is identified as a suitable parameter to influence the product distribution in 1-pentene cracking. An evaluation of selectivies at different reaction conditions shows that high propene yields can only be obtained at high temperatures, but always in combination with high ethene yields. To decouple the formation of propene from the formation of ethene, a reactor with two equally large temperature zones is proposed. Reaction conditions in the two zone reactor are optimized using the single-event kinetic model with the aim to maximize the propene yield at high conversions of the feed at a minimized ethene yield. The results of the optimization are shown in figure 1, leading to a temperature of 580 K in the first and 800 K in the second zone of the reactor.



Figure 1: Comparison of optimized two zone reactor (middle) to one zone reactors with temperature of lower (left) and higher reaction zone (right).

Further work will include the consideration of a recycle reactor for the catalytic cracking of olefins on ZSM-5. Hereby, the reactor outlet stream is separated into  $C_4^{=}-C_{12}^{=}$ -olefins and the product stream consisting of propene and ethene. The  $C_4^{=}-C_{12}^{=}$ -olefins are recycled to the reactor inlet. Since the product stream only contains propene and ethene in this reactor configuration, the 1-pentene feed can be selectively converted to these lower olefins. The model of a reactor for olefins cracking with recycle will be used to optimize the reaction conditions with the aim of maximizing the propene yield.

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# KINETICS AND COMPOSITION OF GREEN OIL FORMED IN SELECTIVE HYDROGENATION OF ACETYLENE OVER A COMMERCIAL Pd-Ag/ Al<sub>2</sub>O<sub>3</sub> CATALYST

Jian Zhang, Hongqiang Pang, Zhijun Sui<sup>\*</sup>, Xinggui Zhou, Weikang Yuan East China University of Science and Technology– Shanghai Shanghai, 200237 China

## Abstract

The green oil formed in selective hydrogenation of acetylene has deleterious effect on the catalyst activity and reactor operation stability. The green oil produced under different operation conditions is captured and characterized by thermal gravimetric, pyrolysis GC-MS, element analysis, Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). C8~C30 straight-chain paraffins and olefins with even numbers of carbon atoms are detected as the main component of green oil. The total amount of green oil increases with the increasing operating time, temperature and partial pressure of hydrogen and acetylene. The molecular weight of green oil resided on the catalyst increases with increasing operation time, temperature and partial pressure of hydrogen, but with decreasing acetylene concentration. A mechanism and kinetic model for green oil formation is proposed based on the characterization results and a micro-kinetic analysis of acetylene hydrogenation over Pd surface.

## Keywords

Green oil, composition, mechanism, kinetics, commercial Pd-Ag catalyst

## Introduction

When producing ethylene in the steam cracking process, a certain amount of acetylene is also produced. It should be removed for downstream ethylene conversion and the mostly adopted process is selective hydrogenation over supported Pd catalyst [1]. In this process, green oil is formed and accumulates on the catalysts, gradually covers the active surface of the metal particles, causing catalyst deactivation and affects the operation stability [2].

The understanding of green oil formation is the key for building deactivation kinetics for this process as well as developing new catalysts. However, the specific composition of green oil has been less reported. Yayun et al. presented that oligomers has an H: C ratio of about 1.9 [4], but most of the details of their experimental procedure were not reported. Sarkany et al. confirmed the presence of carboxylic acids in the oil by infrared and NMR measurements [2]. The oligomers are a complex mixture of mainly unsaturated aliphatic hydrocarbons, which generally range from C4 to C24 but can be as high as C60+[2, 3, 3]5]. All of these results were obtained for the green oil formed over mono-metallic Pd catalyst. Due to the lack of related knowledge, a simplified reaction, acetylene dimerization to 1, 3-butadiene, is used to represent the green oil formation reaction in several kinetic studies of acetylene hydrogenation [6].

In this work, hydrogenation of acetylene over a commercial Pd-Ag/Al<sub>2</sub>O<sub>3</sub> catalyst was carried out under different operation conditions coincide with industrial practice to investigate the kinetics and composition of the green oil. The green oil was fully captured and characterized with different methods, in which the pyrolysis GC-MS was not adopted in the precedent research. Moreover, the green oil formation mechanism and kinetics was proposed based on these results as well as a micro-kinetic analysis of acetylene hydrogenation over Pd surface.

## Experimental

#### Catalyst

The catalyst (BC-H-20B) used in this work contains 0.03wt %Pd and 0.12wt %Ag on an  $Al_2O_3$  carrier (BET surface area=15m<sup>2</sup>/g, pore volume=0.51 cm<sup>3</sup>/g).

#### Catalyst Tests

The selective hydrogenation reaction was carried out on an Altamira  $\mu$ BenchCAT reactor system, in which a stainless steel isothermal tubular reactor was adopted. In each experiment, 0.04g catalyst diluting with 0.12g silica sand was used and reduced in situ at 150 °C for 2 h in a flow of 40mL/min hydrogen and nitrogen. The experiments were carried out under the following operation condition range (The details were listed in Table 1): 0.85~1.5 vol% C<sub>2</sub>H<sub>2</sub>, 0.8~1.8 vol%

<sup>•</sup> Corresponding author.

<sup>•</sup> Email address: zhjsui@ecust.edu.cn

H<sub>2</sub>, 60~90 vol% C<sub>2</sub>H<sub>4</sub>, Temperature, 60~100 °C, operating time, 5~60 h. A total gas flow of 120 mL/min was used N<sub>2</sub> as the balance gas. The pressure of the reactor was kept at 21bar for all experiments. The compositions of the reactant stream, N<sub>2</sub>, H<sub>2</sub>, C1-C4 hydrocarbons, were analyzed by using a four channel micro-chromatograph (micro GC 3000, Inficon, USA).

## Collection of green oil

The green oil generated during the acetylene hydrogenation could accumulate over catalysts or flow out of the reactor together with the reaction stream. So, a condensate adsorption bed which was charged of  $Al_2O_3$  balls was connected after the reactor. The experimental apparatus is showed in Figure 1.



Figure 1. Schematic diagram of the experimental apparatus

## Green oil characterization

TG measurements were carried out in a thermobalance (Pyris 1 TGA) to quantification of the green oil accumulated on the catalyst and captured by the Al<sub>2</sub>O<sub>3</sub> balls. Three to ten milligram samples were placed on a sample holder. After 1h drying at 80 °C, air was introduced and the chamber was heated up from 18 °C to 800 °C with a ramp of 10 °C/min. Pyrolysis GC-MS (Agilent 7890A GC/5975C MSD) equipped with a HP-5MS column was used to investigate the composition of green oil. The sample was heated at 600 °C and analyzed. The composition was determined by matching the NIST database. The elemental analysis was obtained by an energy dispersive X-ray Elementar analyzer (Vario EL III). X-ray photoelectron spectroscopy (XPS) was performed on a Kratos XSAM-800 instrument using Al Ka X-ray with 1486.6 eV as the excitation source. The binding energy of C 1s (284.6 eV) was taken as a reference to correct the binding energies of the samples. Raman analysis was performed at room temperature under ambient conditions on a Renishaw in Via + Reflex Raman spectrometer with a 514.5 nm Ar-ion laser beam.

To investigate the effect of reaction conditions on the composition of green oil, some experiments were designed and the conditions are listed in Table.1.

Tab	ne I. Cataly	st test exper	rimental ce	onditions	
amplag	C.U.(0/)	<b>U</b> .(0/)	C.U.(	$\mathbf{T}(0\mathbf{C})$	

6

Samples	$C_2H_2(\%)$	$H_2(\%)$	$C_2H_4(\%)$	I(°C)	t(n)	
1 <sup>C</sup> , 1 <sup>A</sup>	1.15	1.8	90	80	5	•

$2^{\rm C}, 2^{\rm A}$	1.15	1.8	90	80	12
3 <sup>°</sup> , 3 <sup>A</sup>	1.15	1.8	90	80	36
4 <sup>°</sup> , 4 <sup>A</sup>	1.15	1.8	90	80	60
5 <sup>°</sup> , 5 <sup>A</sup>	1.15	1.8	90	60	12
6 <sup>C</sup> , 6 <sup>A</sup>	1.15	1.8	90	70	12
7 <sup>°</sup> , 7 <sup>A</sup>	1.15	1.8	90	90	12
8 <sup>°</sup> , 8 <sup>A</sup>	1.15	1.8	90	100	12
9°, 9 <sup>a</sup>	1.15	1.8	60	80	12
10 <sup>°</sup> , 10 <sup>A</sup>	1.15	1.8	70	80	12
11 <sup>°</sup> , 11 <sup>A</sup>	1.15	1.8	80	80	12
12 <sup>°</sup> , 12 <sup>A</sup>	1.15	0.8	90	80	12
13 <sup>°</sup> , 13 <sup>A</sup>	1.15	1.0	90	80	12
14 <sup>°</sup> , 14 <sup>A</sup>	1.15	1.3	90	80	12
15 <sup>°</sup> , 15 <sup>A</sup>	0.85	1.8	90	80	12
16 <sup>°</sup> , 16 <sup>A</sup>	1.3	1.8	90	80	12
17 <sup>°</sup> , 17 <sup>A</sup>	1.5	1.8	90	80	12
18 <sup>°</sup> , 18 <sup>A</sup>	1.8	1.8	90	80	12

<sup>C</sup> indicating green oil accumulated on the catalyst

<sup>A</sup> indicating green oil adsorbed on Al<sub>2</sub>O<sub>3</sub> balls

## Results

## Thermal gravimetric analysis

The quantities of the green oil on the samples were measured by TG and some typical results were shown in Figure 2(a). Obvious weight loss before 600°C could be observed. The DTG curves were also shown in Figure 2(b). Three peaks could be found for the  $2^{A}$  sample and two peaks for the  $2^{C}$  samples. Since, the peak centered at around 120 °C was also observed on the fresh alumina adsorbent, only peak above 250 °C was ascribed to the loss of the green oil and the amount was obtained by integrated the corresponding peak area.



Figure 2. TG and DTG results of Al<sub>2</sub>O<sub>3</sub> balls and used catalyst

Reaction conditions: 1.8% H<sub>2</sub>, 1.15% C<sub>2</sub>H<sub>2</sub>, 90% C<sub>2</sub>H<sub>4</sub>, P= 21bar, T= 80°C, operating time=12h



Figure 3. Weight of green oil as a function of (a)operating time and (b)C<sub>2</sub>H<sub>2</sub> partial pressure

4/1)

## Reaction conditions: (a) 1.8% H<sub>2</sub>, 1.15% C<sub>2</sub>H<sub>2</sub>, 90% C<sub>2</sub>H<sub>4</sub>, P= 21bar, T= 80°C,;(b) 1.8% H<sub>2</sub>, 90% C<sub>2</sub>H<sub>4</sub>, P= 21bar, T= 80°C, operating time=12h

Some typical results of the green oil amount were shown in Figure 3. Figure 3(a) showed the weight of green oil almost increases linearly in the operating time from 5 to 60h. Figure 3(b) presented the amount of green oil as a function of partial pressure of  $C_2H_2$ . The amount of green oil increases with the partial pressure of  $C_2H_2$  upto a  $C_2H_2$  partial pressure of 1.5 vol% and then increase slowly. It was also observed (The results were not shown here) that the amount of green oil increases with the decreasing of hydrogen partial pressure and the  $C_2H_4$  concentration has no apparent influence on the green oil amount.

## Pyrolysis GC-MS analysis

The green oil composition distribution was determined from pyrolysis GC-MS results Most of the peaks have been positively identified. To testify if the results were correct, a mixed standard sample was measured. Figure 4 shows the pyrolysis GC-MS chromatogram of the standard sample and sample 7<sup>C</sup>. The results demonstrate the composition matched to spectra in the MS library file is accurate. C8~C30 straight-chain n-paraffins and  $\alpha$ -olefins with even numbers of carbon atoms were detected as the main component in green oil on the catalyst. In addition, numerous branched paraffins, linear and branched mono-olefins, and some cycloalkanes and aromatics are detected.



Figure 4. Standard sample and green oil on the catalyst sample chromatogram from pyrolysis GC-MS Reaction conditions: 1.8% H<sub>2</sub>, 1.15% C<sub>2</sub>H<sub>2</sub>, 90% C<sub>2</sub>H<sub>4</sub>, P= 21bar, T= 90°C, operating time=12h.

Figure 5 showed the composition distribution of green oil on the catalyst (a) and  $Al_2O_3$  balls (b) obtained under different operating time. The composition of green oil accumulated on the catalyst has a longer chain and the green oil on the  $Al_2O_3$  balls has more olefins. The composition distribution of green oil on the catalyst is predominately normal paraffins of even numbers, from C12 to C28, and the composition distribution of green oil on the  $Al_2O_3$  balls is mainly normal olefin of even numbers from C10 to C16. Figure 5(a) shows that the carbon number of maximum product increase with the operating time, from C14 to C22 while the operating time increase from 5 to 60h. But there is not a significant composition distribution change on the  $Al_2O_3$  balls.





Figure 5. Composition distribution of green oil with different operating time on catalyst (a) and Al<sub>2</sub>O<sub>3</sub> balls (b). Reaction conditions: 1.8% H<sub>2</sub>, 1.15% C<sub>2</sub>H<sub>2</sub>, 90% C<sub>2</sub>H<sub>4</sub>, P= 21bar,  $T=80^{\circ}C$ .

The composition distribution of green oil formed under different reaction temperature on the catalyst (a) and Al<sub>2</sub>O<sub>3</sub> balls (b) were shown in Figure 6. The composition distribution of green oil on the catalyst are predominately normal paraffins of even numbers, from C8 to C28 and the composition distribution of green oil on the Al<sub>2</sub>O<sub>3</sub> balls is mainly normal oleffins of even numbers, from C8 to C18. Figure 6 (a) shows that the carbon number of maximum product increase with the reaction temperature, from C18 to C24 while the reaction temperature increase from 60 to 100 °C. But there is not a significant composition distribution change on the Al<sub>2</sub>O<sub>3</sub> balls.



Figure 6. Composition distribution of green oil with different reaction temperature on catalyst (a) and  $Al_2O_3$  balls (b). Reaction conditions:  $1.8\%H_2$ ,  $1.15\%C_2H_2$ ,  $90\%C_2H_4$ , P=21bar, operating time=12h.

It should also be noted that the carbon numbers of the green oil accumulated on the catalyst increases with the decreasing of  $C_2H_2$  partial pressure and the increasing of  $H_2$  partial pressure and keeps constant when the  $C_2H_4$  partial pressure changes. The composition of green oil adsorbed on the alumina balls is not varied for all the samples.

## Elemental analysis

Table.2 Elemental analysis of green oil								
Samples	Weight(mg)	C%	Н%	H/C				
4 <sup>C</sup>	2.351	6.02	0.68	1.49				
	2.354	5.68	0.60	1.33				
16 <sup>C</sup>	2.306	4.89	0.52	1.28				
	2.289	5.24	0.57	1.30				

The results of elemental analysis of the green oil on the catalyst are listed in Table 2 in terms of H/C ratio. The average H/C ratio of green oil on the catalyst is 1.35. The result indicates that there are some unsaturated hydrocarbons consisting in the green oil. The sample  $16^{C}$  has a lower H/C ration indicating more C=C bonds exist in this sample.

The C 1s XPS spectra (not shown here) of green oil are fitted with Gaussian curves to elucidate their structures. There exist two distinct Gaussian peaks centered at 284.5 and 285.6eV, which are correspond to C–C, C=C, respectively. Therefore, the

area ratio of these two peaks indicates the amount ratio of C–C and C=C. The result is C–C/ C=C ratio around 2. Then the H/C ration could be calculated around 1.8, which is similar to the elemental analysis results. It is also found that more C=C bond exist in the sample obtained at higher  $C_2H_2$  partial pressure and lower  $H_2$  partial pressure.

## Green oil formation mechanism and kinetics

From the results stated above, we notice that the composition of green oil adsorbed on the alumina balls has more unsatured content and do not varied with the change of the operation conditions. Since this kind of green oil has less contact time on the catalyst surface, it should be close to the primary products of the green oil formation reaction. The newly formed green oil is olefins in nature and secondary hydrogenation, isomerization and aromatization reaction occur when it is accumulated on the catalyst.

To elucidate the origination of the green oil, a micro-kinetic simulation of hydrogenation of acetylene over Pd catalyst was carried out by using DFT results obtained by Norskov et al. [7] as the primary kinetic parameters source. It is found that  $C_2H_3^*$  and  $H^*$  are the most abundant surface species and the variation of these species' surface coverage with different operation conditions has a good agreement with the amount of green oil. Then, the green oil should be formed by polymerization of  $C_2H_3^*$ .

The kinetic model of the green oil formation is under exploration for now.

## Conclusions

C8~C30 straight-chain paraffins and olefins with even numbers of carbon atoms are detected as the main component of green oil. Some branched paraffins, linear and branched mono-olefins, and some cycloalkanes and aromatics are also detected. More long chain paraffins and olefins are generated when the operating time, temperature and partial pressure of hydrogen increase. However, the compositions of green oil are almost similar when different ethylene partial pressure is adopted. The green oil should be formed by polymerization of  $C_2H_3^*$ .

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# MODELING THE REMOVAL OF SULFUR, AROMATICS AND HEAVIER FRACTION OF SCRAP TIRE PYROLYSIS OIL (STPO)

Idoia Hita<sup>\*1</sup>, Martin Olazar<sup>1</sup>, Javier Bilbao<sup>1</sup>, Jose María Arandes<sup>1</sup> and Pedro Castaño<sup>1</sup> <sup>1</sup>University of the Basque Country UPV/EHU, Dep. Chemical Engineering, P.O. Box 644, 48080 Bilbao (Spain)

## Abstract

The upgrading of scrap tire pyrolysis oil (STPO) has been studied in order to enhance its composition by means of hydrotreating, removing (i) sulfur, (ii) aromatics, and (iii) gasoil lump (BP > 350 °C). The main goal is increasing its potential towards being used as a blend in the refinery. Particularly, the interest has been focused in the hydrodesulfurization (HDS), hydrodearomatization (HDA) and mild hydrocracking (MHC) reaction pathways, using a commercial NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst. The hydrotreating runs have been carried out in a downflow fixed bed reactor working in trickle bed regime at time on stream, 0-8 h; temperature, 300-375 °C; pressure, 65 bar; and space time, 0-0.5 g<sub>cat</sub> h g<sub>feed</sub><sup>-1</sup>. Under these conditions, negligible deactivation has been observed and data in the steady state of the catalyst have been reported. Based on previously reported kinetic models, three models for the different reaction pathways (HDS, HDA and MHC) have been proposed to describe the evolution of the sulfur species, composition fractions and product lumps in the hydrotreating of STPO at different experimental conditions. The corresponding kinetic parameters have been computed by means of a program developed in Matlab, and applied in further simulations.

## Keywords

Hydrotreating, Kinetics, Scrap Tires.

## Introduction

The energetic dependence in fossil energy sources of developed countries together with petroleum depletion is turning the utilization of alternative energy sources into a major issue. Waste refinery aims for the production of fuels and chemicals from wastes, within of which the valorization of scrap tires is becoming a major driving force for research and innovation.

Additionally to the already existing routes for scrap tire recovery (material, energy or chemical recovery) (Sienkiewicz et al., 2012), an emerging pyrolysis route is attracting increasing interest due to its versatility, minimal emission of pollutants, and promising features for its implementation in a large scale (Lombardi et al., 2015; Williams, 2013).

Pyrolysis products are divided into three main fractions: gas, liquid (oil) and solid. The liquid fraction is the most economically and energetically attractive, and is commonly referred to as scrap tire pyrolysis oil (STPO). This STPO is a complex mixture of hydrocarbons with a high calorific value (Roy and Chaala, 2001), encouraging for its use as an alternative fuel. However, its composition shows some relevant barriers that hinder its direct use in internal combustion engines (Zabaniotou et al., 2003). The main limitations affecting the implementation of STPO as an alternative fuel can be summarized as for the high amount of (i) sulfur and other heteroatomic molecules (mainly benzothiazole, BTZ; and dibenzothiophenes, DBTs), (ii) heavily condensed aromatics and (iii) molecules within the gasoil boiling point range (> 350 °C).

Hydroprocessing appears as the key refinery process that allows for solving these STPO issues and increasing the value of the feedstock (Furimsky, 1998). The three particular reaction routes for each upgrading goal are: hydrodesulfurization (HDS), hydrodearomatization (HDA) and mild hydrocracking (MHC). HDS kinetics can be explained by the Langmuir-Hinshelwood (LH) expression, as the most common form for heterogeneous catalysis. For MHC and HDA, the lumping technique is a common approach based in grouping the compounds of a complex mixture according, in this case, to either a boiling point or a group reactivity criteria

Considering all the previous, hydrotreating has been proposed for the upgrading of STPO, focusing this work in the modeling of the (i) HDS, (ii) MHC and (iii) HDA routes using a NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst, whose good performance has been proved in a previous catalyst screening (Hita et al., 2015). Different types of kinetic mechanisms have been proposed for further computation of the kinetic parameters. Lastly, and from these computed values, a simulation of the evolution of the conversion for the three reaction routes has been carried out for different space time and temperatures, in order to establish the optimal operating conditions.

#### Experimental

The hydrotreating runs have been carried out in a down-flow fixed bed reactor working in trickle bed regime. The experimental conditions were: time on stream (TOS), 0-8 h; space time, 0-0.5  $g_{cat} h g_{feed}^{-1}$ ; temperature, 300-375 °C; pressure, 65 bar; H<sub>2</sub>/Oil ratio of 1000 vol%. The catalyst (diluted in CSi) is loaded in the reactor following the procedure described by Van Herk et al. (2009). Prior to the reaction the catalyst is sulfided in-situ with 5 mL min<sup>-1</sup> of a H<sub>2</sub>S:H<sub>2</sub> mixture (10 vol%) rising the temperature at 5 °C min<sup>-1</sup> up to 400 °C and maintaining that temperature for 4 h. Liquid product samples are collected every 1 h and analyzed via bi-dimensional gas chromatography coupled with mass spectroscopy (GCxGC-MS). The outlet flow of the sample and carrier is connected to a Flame Ionization Detector (FID) and a Mass Selective Detector (MSD). The sulfur in the products has been analyzed by means of gas chromatography using a Pulsed Flame Photometric Detector (PFPD). Sulfur content has been determined based in a calibration line  $(R^2 > 0.995)$  using a benzothiazole standard (Aldrich, 96 %).

STPO consists of 25.7 wt% naphtha (35-215 °C), 44.5 wt% diesel (215-350 °C) and 29.8 wt% gasoil (> 350 °C), as measured by GCxGC-MS. Based on a chemical group classification, STPO can also be divided into: 2.39 wt% paraffins and isoparaffins (P+iP), 7.11 wt% olefins (O), 34.37 wt% naphthenes (N), and 55.83 wt% aromatics (A<sub>1</sub> and A<sub>2</sub>). Elemental sulfur in STPO accounts for 11,600 ppm, with benzothiazole (BTZ) being the main sulfur-containing compound (3,794 ppm), and the rest of the sulfur appearing in the form of dibenzothiophenes (DBTs), which have been classified according to the number of C atoms in their substituents, as follows: M<sub>1</sub>DBT, 182 ppm; M<sub>2</sub>DBT, 752 ppm; M<sub>3</sub>DBT, 3,460 ppm; and M<sub>4</sub>DBT, 3,412 ppm, respectively.

The kinetic parameters for the three reaction routes at the reference temperature of 390 °C have been computed by developing a program in Matlab software, and minimizing the square error between the experimental data and the data predicted by the model.

## **Results and Discusion**

Langmuir-Hinshelwood type of mechanism is the most common form of expression for HDS kinetics (Ancheyta, 2011). In the HDS approach, the removal of the different sulfur species has been modeled (Figure 1a). In our case, the inhibition effect of the H<sub>2</sub>S formed as a byproduct has been considered in the kinetic equation, together with the H<sub>2</sub> concentration in the media. For MHC, a sequential scheme considering gasoil↔diesel and diesel↔naphtha transformations with an additional gasoil-naphtha stage has been proposed (Figure 1b). A similar sequential kinetic scheme has been proposed for HDA reactions (Figure 1c) with transformations from the heaviest to the lightest molecules  $(A_2 \leftrightarrow A_1 \leftrightarrow N \leftrightarrow P + iP)$ and an additional  $A_1 \rightarrow P+iP$  transformation.



Figure 1. Kinetic schemes used for describing the a) HDS, b) MHC and c) HDA reaction pathways in the hydrotreating of STPO.

The evolution of the different sulfur species with space time for different temperature conditions (both experimental and model fitting data) is shown in Figure 2. As for these results, the accuracy of the LH type of model for predicting the evolution of HDS reactions has been evidenced.



Figure 2. Experimental data (dots) and model fitting (lines) for the evolution of a) M<sub>1</sub>DBT, b) M<sub>2</sub>DBT, c) M<sub>3</sub>DBT and d) M<sub>4</sub>DBT with space time in the HT of STPO.

An increase in space time (and therefore in the amount of catalyst loaded in the reactor) significantly affects sulfur removal, obtaining the highest removal rates at the higher space times. Considering the original sulfur distribution in STPO (previously specified) and the most favorable HDS conditions (375 °C and 0.5  $g_{cat}$  h  $g_{feed}^{-1}$ ), the M<sub>4</sub>DBT species (Figure 2d) are the ones that have been removed in a greater extent, with individual conversions of 95-99 %, followed by M<sub>1</sub>DBT and M<sub>2</sub>DBT (92-98 %) (Figure 2a,b) and with

 $M_3DBT$  species (Figure 2c) being the most difficult to eliminate (85-97 %). The lowest HDS reactivity of more substituted DBT species has been reported in a previous work (Hita et al., 2015). However, according to these results the removal of M<sub>4</sub>DBT occurs faster than that of M<sub>3</sub>DBT species. From this, the determining role of the substituent position is evidenced, since substituent groups located in close to the C-S bond can strongly hinder HDS (Song and Ma, 2003). Considering this, it can be deduced that the methyland ethyl groups in the remaining M<sub>3</sub>DBT are located in positions 4- and 6- of the molecule (the closest to the S atom), while M<sub>4</sub>DBT species have a lower proportion of molecules with substituents in these positions and can be removed faster.

The computed parameter values are listed in Table 1 for the different hydroprocessing route models proposed. The kinetic constant values obtained for HDS predict that  $M_4DBT$  occurs the fastest, followed by  $M_1DBT$  and  $M_2DBT$  (with a very similar rate), and a lower reactivity of  $M_3DBT$  species. Even though removal of  $M_4DBT$  was expected to occur the slowest, it has occurred twice as rapid as that of  $M_3DBT$  due to the position of their substituents.

 Table 1. Kinetic parameters for the hydrotreating models.

	k, T <sub>ref</sub> 390 °C	Ea
	(gfeed gcat <sup>-1</sup> h <sup>-1</sup> )	(kJ mol <sup>.</sup> 1)
M <sub>1</sub> DBT	2.10·10 <sup>-5</sup>	34.30
M <sub>2</sub> DBT	1.89·10 <sup>-5</sup>	33.49
M <sub>3</sub> DBT	$1.44 \cdot 10^{-5}$	36.10
M <sub>4</sub> DBT	2.79·10 <sup>-5</sup>	32.38
Gasoil→Diesel, k1	10.23	11.83
Diesel→Gasoil, k-1	4.08	1.87
Diesel→Naphtha, k₂	4.95	2.90
Naphtha→Diesel, k-2	9.83	0.57
Gasoil→Naphtha, k <sub>3</sub>	7.79	12.60
Hydrogenation, k <sub>1</sub>	3.71·10 <sup>2</sup>	0.61
Dehydrogenation, k-1	$1.49 \cdot 10^{2}$	
Hydrogenation, k <sub>2</sub>	$1.57 \cdot 10^{2}$	92.01
Dehydrogenation, k-2	$1.66 \cdot 10^{2}$	
Ring opening, k <sub>3</sub>	$1.71 \cdot 10^{2}$	22.78
Cyclization, k-3	16.3	
Chain Scission, k4	1.71	69.73

Regarding MHC, the evolution of product lumps with space time at 375 °C is displayed in Figure 3, obtaining an accurate fitting assuming the sequential kinetic scheme of Figure 1b. Diesel is the most abundant lump at all conditions, with significant variations below 0.3  $g_{cat}$  h  $g_{feed}$ <sup>-1</sup>, range in which diesel yield increases (9 wt% more) and gasoil yield decreases (12 wt% less), but with marginal variations in naphtha yield, especially at lower temperatures. The most favorable conditions from all the studied for obtaining higher naphtha and diesel yields have been 375 °C and 0.5  $g_{cat}$  h  $g_{feed}$ <sup>-1</sup>, equally to what happened in HDS reactions. According to these results, at the entrance of the reactor products consist mainly of gasoil and diesel but, in further positions naphtha becomes more relevant.

According to the kinetic parameters summarized in Table 1 for the proposed HC kinetic model, the transformation of gasoil into diesel is favored over its reverse reaction,  $(k_1 > k_{-1})$ , while transformation of diesel into naphtha is less favored and very little amounts of compounds within this lump are being formed. Kinetic constants predict that the slight increase in the naphtha yield occurs mainly due to the hydrogenation and cracking of compounds originally present in gasoil.



Figure 3. Experimental data (dots) and model fitting (lines) for the evolution of product lumps with space time in the HT of STPO at 375 °C.

Figure 4 shows the evolution with space time of the compositional fraction of products at 340 °C. Considering the original composition of STPO, complete hydrogenation of the olefinic fraction (O) has been achieved, as well as partial hydrogenation of aromatics and further ring opening of naphthenics, which has been reflected in a very significant increase of paraffinic compounds (from 2.4 wt% in STPO to 33 wt%), and a decrease in the rest of fractions (particularly aromatics). Furthermore, higher amounts of paraffinic compounds have been obtained upon increasing hydrocracking temperature.

From the kinetic parameters listed in Table 1 for the HDA model, and according to the values of  $k_1$ ,  $k_1$  and  $k_2$ , it can be deduced that hydrogenation of 2ring aromatics represents for the most relevant reaction, occurring more rapidly that its reverse reaction  $(k_2 > k_2)$ . However, in the same conditions, the reversibility of A<sub>1</sub> aromatic hydrogenation is more favored towards dehydrogenation  $(k_2 < k_2)$ . Due to the low cracking ability of the catalyst, ring opening and aliphatic chain scission reactions occur in a much lesser extent, as deduced from their constant values.



Figure 4. Experimental data (dots) and model fitting (lines) for the evolution of composition fractions with space time in the HT of STPO at 340 °C.

The computed values listed in Table 1 have allowed for simulating the evolution of the conversion of the three hydroprocessing reactions routes. As an example, the corresponding simulation for HDA conversion is displayed in Figure 5.





The obtained results have evidenced the enhancing effect of space time for the three hydroprocessing goals. However, temperature affects each reaction pathway differently, since in the case of HDA reactions it displaces the hydrogenation equilibrium for aromatic compounds in such a way that, at higher temperatures, lower amounts of aromatics are being removed. From the simulations, and in order to satisfy a conversion compromise between the different hydroprocessing goals, the optimal operation conditions have been established as:  $350-360 \,^{\circ}$ C and 0.2-0.3 g<sub>cat</sub> h g<sub>feed</sub><sup>-1</sup>.

#### Conclusions

The suitability of the LH-type of kinetic mechanism for HDS and the proposed kinetic schemes for MHC and HDA has been proved for obtaining accurate predictions for the evolution of the three hydrotreating reaction routes at different experimental conditions. Increasing both temperature and space time favor the removal of sulfur and allow for obtaining lighter product lumps. However, regarding product composition, and due to strong thermodynamic effects, higher removal of aromatics is achieved at lower temperatures due to the displacement of hydrogenation equilibriums of aromatics. Therefore, for determining the optimal operating conditions, a compromise between the different hydroprocessing goal must be established.

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# LIQUID KINETIC STUDY OF THE CATALYTIC CRACKING OF WASTE MOTOR OIL FOR OBTAINING DIESEL LIKE FUELS

Diana C. Vargas<sup>a</sup>, María B. Alvarez<sup>a</sup> and Daniela Almeida Streitwieser<sup>a,\*</sup> Kevin M. Van Geem<sup>b</sup>

 <sup>a</sup> Universidad San Francisco de Quito USFQ, Departamento de Ingeniería Química, Laboratorio de Desarrollo de Energías Alternativas (LaDEA), Quito D.M., Ecuador 170157
 <sup>b</sup>Laboratory for Chemical Technology, Ghent University, Technologiepark 914, 9052 Gent, Belgium

## Abstract

Considering the serious impact caused to the environment by the inappropriate disposal of waste motor oils, it is vital to find alternative mechanisms to handle and dispose these wastes in a controlled process. The reuse of waste motor oil as an energy source for the synthesis of diesel like fuels provides an alternative way for the disposal of this residue in a feasible, sustainable and environmental responsible way (Tamunaidu & Bhatia, 2007) (Audibert, 2006) (Bridjanian, 2006). This project addresses the kinetic study of the catalytic cracking of waste motor oils using mesoporous aluminum-silicate zeolites doped with Zinc in 1% to 2%. The study was performed in a batch reactor and the catalysts were added in a volume ratio of 1%. Both the waste motor oil and the fuel like product were characterized according to ASTM standards to ensure an adequate characterization and to guarantee the proper quality of the product. The results from the overall kinetic study show that the cracking reaction can be described by using a first order kinetic law with respect to the used motor oil. The activation energy for the thermal catalytic cracking is of 370.43 [kJ/mol], which explains the high energy required for the process, and it is reduced to 287.37 [kJ/mol] when the alumina-silicates catalysts are used. Also the overall yield of the process is increased from 0.63 to 0.90 during the catalytic reaction.

## Keywords

Catalytic cracking, waste motor oil, synthetic fuel, diesel like fuel, alumina-silicates, meso-porous zeolites

## Introduction

The continuous extraction of the energetic resources has allowed the vast development of the actual highly technified society. However, the dilemma appears on how this accelerated pace can be maintained without destroying the environment (Tamunaidu & Bhatia, 2007). In this context the need to find new sources of alternative energies has appeared. One option is the development of renewable energies, which are virtually inexhaustible and regenerate naturally, but crops need to be cultivated for this purpose. Another option is the energetic utilization of industrial, agricultural or municipal wastes. This process not only reduces the extraction of fossil fuels, but also the amounts of waste that need to be managed(R. Kothari, 2010).

Annually lubricating oils constitute 1% of the total demand for oil industry and approximately 50% of lubricant oils are used for the automotive industry (Maher, 2011). Given that only in 2014 worldwide, more than 80 million cars were sold (LeBeau, 2014), it is vital to control and manage these residues. The lubricating motor oil in vehicles need to be changed regularly, since the high temperatures and friction in the motor degrades and contaminates the oil with heavy metals, soot and aromatic hydrocarbons (ONU, United Nations Environment Programme)

Nowadays the ordinance 067 in the article Art.II.383c of the Municipality of Quito establishes that all the used motor oil must be stored in tanks with lids and neatly labelled "used oil", and that the final destination of these containers must be determined through the Metropolitan Environmental Management Direction and Biofactor S.A. (DMQ, 2002). At the moment this waste is incinerated in cement plants causing a high atmospheric contamination index (Almeida Streitwieser et al., 2011).

On the other hand the energetic content of the used motor oil is extremely high, making it an excellent source to produce secondary fuels (Almeida Streitwieser et al., 2011). Therefore, it is necessary to develop new environmentally friendly treatment methods to take advantage of the potential use of waste motor oil as fuel. For this reason at the Laboratory for Development of Alternative Energies at Universidad San Francisco de Quito, LaDEA, has focused its research on the feasibility analysis of producing light fuels from waste lubricating oils by thermal and catalytic cracking (Almeida Streitwieser., 2011. Previous studies determined that the use of aluminum silicates as catalysts attains a cracking reaction at lower temperatures to those in thermal cracking (Benedik & Almeida, In progress).

In this investigation the catalytic cracking process that takes place in a batch reactor without agitation will be presented. The main goal is to determine the kinetic data for the catalytic cracking reaction by modifying the cracking reaction temperature and measuring the concentration change over time.

## **Materials and Methods**

## Reagents

The waste motor oil was supplied by a collection station in Quito, where the oil is collected on a daily basis. The reagents used for the experimental

<sup>\*</sup> Corresponding author: dalmeida@usfq.edu.ec

section were: Tetraethyl orthosilicate (TEOS) (98% purity) and triton X-114 (laboratory grade) by Sigma-Aldrich Chemicals, aluminium tri-sec-butylate (TBA) (97% purity) and hydrochloric acid fuming 37% (GR for analysis) by Merck Chemicals and zinc chloride (97.1% purity) by J.T. Baker and were bought from Laboratorio de Reactivos H.V.O. (Quito, Ecuador). All the chemicals were used in the conditions they were received.

## Cracking process

The cracking process includes three steps: pretreatment of the waste motor oil, cracking reaction and post-treatment. Figure 1 shows a block diagram of the process.



Figure 1 Block diagram of the catalytic process

#### Pre-treatment

The waste motor oil has to undergo a pretreatment prior to the cracking process. These pretreatment aims the elimination of any water residues or solids by heating the sample at 100°C for at least 24 hours and filtering the sample respectively..

#### Cracking reaction

The equipment used for the thermal and catalytic cracking of the waste motor oil is a 250 mL glass batch reactor placed in the Precision Scientific Petroleum Herzog silt with a maximum power of 1100 Watts. For the thermal and the catalytic cracking experiments 100 g of the pre-treated waste motor oil is placed in the batch reactor with 1 g of catalyst. The catalysts used in this study are prepared as directed for Hidrobo, A. and Benedik and Almeida in progress. The aluminum-silicates, are synthesized in the Laboratory of Chemistry and Chemical Engineering of the Universidad San Francisco de Quito. The flask with the sample is agitated and placed in the cracking equipment. During the first 20 minutes the power of the equipment is set to 50% of its full power and then increased with a ramp of 10 Watts per hour. The condensate from the cracking reaction is collected in the receiver cylinder and weighted. The condensate volume is registered as a function of temperature.

After the cracking reaction, the product undergoes into a rectification process that yields three different fractions; one of them is the desired final product. These fractions are separated according to their bubble point temperature range. The desired product is collected at bubble temperature between  $149^{\circ}$ C and  $360^{\circ}$ C.

### Kinetic study

The model used for the study of the kinetics of the cracking reactions for waste motor oil was the classical potential law model, where the reaction rate is a function of concentration. This expression is presented in Eq. 1 and can be linearized to obtain the kinetic parameters by applying the logarithm.

$$R_A = -k \cdot C_A^n \tag{1}$$

Where k and n are the kinetic constant and the reaction order, respectively.

The cracking reaction of the waste motor oil can be described as presented in Eq. 2.

$$C_{30}H_{62} \rightarrow C_{13}H_{28} + C_{12}H_{24} + C_5H_{10}$$
(2)

Where the desire product are the hydrocarbons with a number of carbon atoms between 13 and 12.

Table 1 Characterization methods

Norm	Method	Equipment	
ASTM	Standard Test Method for Flash	Herzog HFP 380	
D56	Point by Tag Closed Cup Tester	Pensky Martens	
ASTM	Standard Test Method for	Precision Scientific	
D86	Distillation of Petroleum Products at	Petroleum	
D80	Atmospheric Pressure	Instrument Herzog	
ASTM D1298	Standard Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method	Hydrometer Precision API	
ASTM D2270	Standard Practice for Calculating Viscosity Index from Kinematic Viscosity at 40 and 100°C	Viscometer CANNON 100 T642, Kohler bath KV3000	
	Standard Test Method for Sulfur in		
ASTM	Petroleum and Petroleum Products	HORIBA SLFA	
D4294	by Energy-Dispersive X-Ray	2800	
	Fluorescence		

## **Results and Discussions**

Before performing the kinetic analysis of the cracking reaction for the waste motor oil it is preheated and characterized. The standards methods and equipment are described in Table 1. The characterization is made to compare it with the final product in order to identify the potential use of it as raw material to obtain commercial diesel like fuel in Table 2. The results of the analysis of the waste motor oil are presented, as well as the acceptable ranges for diesel like fuels. All analysis were conducted at the Laboratory for Quality Control of Clean Products Terminal "El Beaterio" under ASTM standards. The results are shown in Table 2. These values obtained for the waste motor oil are out of range of the requirements for diesel # 2.

The cracking reactions are carried out in a batch reactor of high temperature resistant borosilicate glass. In Figure 3 a) the time dependence of the variation of concentration at different reaction temperatures is presented. It can be observed that at 300-320 °C cracking temperature the reaction rate is small, while it increases drastically at 330 °C. These curves can be modelled as a function of time with equations of the form  $y = -ae^{bx}$  and the value of the parameters a and b and the coefficient of determination  $R^2$  are shown in Table 3. The cracking reaction has been investigated with three different catalysts. The catalysts used in this study for the catalytic cracking of

the waste motor oil were selected from a previous investigation in which it was determined that the matrix of Al / Si doped with Zn at 1 and 2% are the best catalysts for this reaction (Benedik & Almeida, In progress).

Table 2 Characterization of waste motor oil and product from cracking process

-		Flash Point <sup>1</sup> [°C]	Distilla -tion <sup>2</sup> [°C]	API gravity <sup>3</sup> [°API]	Kinematic Viscosity <sup>4</sup> [cSt]	Sulfur content <sup>5</sup> [%p/p]
	Diesel #2	Min 51	Max 288	32-39	2.5-6	Max 0.7
Raw Material	Waste motor oil	69	380	29.6	113.14	0.364
Final product process	Thermal cracking	65	354	37.4	4.65	0.1614
	Catalytic cracking Al/Si	68	342	38.9	4.67	0.1403
	Catalytic cracking Al/Si Zn 1%	69	343	38.5	4.78	0.1305
	Catalytic cracking Al/Si Zn 2%	70	345	39.1	4.72	0.1264

<sup>1</sup> ASTM D56, <sup>2</sup> ASTM D86, <sup>3</sup> ASTM D1298, <sup>4</sup> ASTM D2270, <sup>5</sup> ASTM D4294

These catalysts produce a decrease of the reaction temperature and an increase of the product selectivity.



a) Thermal cracking reaction. b)Catalytic cracking reaction Al/S matrix. c)Catalytic cracking reaction Al/Si matrix doped with Zinc 1%. d) Catalytic cracking reaction Al/Simatrix doped with Zinc 2%.

Figure 2 Concentration of used oil during the reaction

A differential analysis method is used to obtain the kinetic rate law of the cracking reactions. In Figure 4 the linearized form of the potential law model is presented which can be modelled with equations of the form y=mx +b where m represents the reaction order. In Table 4 values for the parameters of the linear equations m, b and R<sup>2</sup> are presented. The value b is the log base 10 value of the kinetic constant. As presented in Table 3 for the thermal cracking reaction a reaction order of 1.0 with an activation energy, Ea, of 370.39 [kJ/mol] has been obtained. The reaction temperature should be between 340 °C and 360 °C to obtain an acceptable conversion of the waste motor oil into the desired product. Between the thermal and catalytic reaction the main difference observed in Table 3 is the decrease in the activation energy. Comparing the thermal cracking with the reaction catalyzed by the Al/Si matrix shows a decrease of 17.82 % and the Al/Si matrix doped with 1% Zn a decrease of 24.21 while the Al/Si matrix doped with 2% Zn shows the largest decrease with a value of 24.84%. Using the kinetic constants obtained for every temperature investigated for the different cracking reactions, Arrhenius Law is used to determine the activation energy and the pre exponential factor.



The linearized diagrams as well as the equations are shown in Figure 5. The conversion grade obtained for the different experiment as a function of the temperature for the cracking reactions are shown in Figure 6.



activation energy of the cracking reactions

It can be observed that for temperatures below 300 °C the cracking reaction cannot take place. For the cracking reactions Figure 6 shows that for temperatures between 300 and 310 the conversion

grade obtained is minimum and the his matrix doped with 2% Zn. For temperatures between 310 and 330 results shown a great difference of nearly 0.6 in comparison of the thermal cracking with the catalytic cracking reaction. Finally, for temperatures between 340 and 360 the maximum conversion is achieved for all the cracking reactions. The maximum conversion for the catalytic reaction is reached at 330°C while the maximum conversion for thermal cracking is reached at 350°C. The catalytic reaction shows a decrease in the reaction temperature by 20°C.

Exposimont	Tomporature [°C]	Differential analysis			Temperature dependence			Kinetic parameters	
Experiment		А	b	$\mathbb{R}^2$	m	b	$\mathbb{R}^2$	n*[-]	Ea**[kJ/mol]
	300	21165	-0.002	0.9814	1.0038	-2.7098	0.9751		
<b>T</b> T1 1	310	200.7	-0.002	0.9751	1.2310	-3.2380	0.9814	10.0176	370.39
Thermal	320	199.59	-0.002	0.9913	0.8022	-2.2447	0.9913	$1.0 \pm 0.176$	
	330	224.5	-0.026	0.9677	0.9859	-1.5738	0.9677		
Al/Si	300	204.02	-0.001	0.8951	0.8876	-2.7453	0.8951		
	310	207.51	-0.001	0.9935	0.8188	-2.5823	0.9935	1.0 ± 0.116	304.39
	320	202.66	-0.003	0.947	0.7154	-2.3449	0.9962		
	330	201.29	-0.033	0.9828	0.9906	-1.4698	0.9828		
	300	200.7	-0.0005	0.904	0.7333	2.6937	0.9821		
41/S; 7n 10/	310	199.78	-0.004	0.9865	0.8405	-2.1516	0.9819	$0.8 \pm 0.126$	280.71
Al/51 Zh 1%	320	188.31	-0.008	0.9837	0.9946	-2.0923	0.9837	0.8 ± 0.120	200.71
	330	237.88	-0.033	0.9914	0.9876	-1.4325	0.9914		
Al/Si Zn 2%	300	201	-0.0006	0.9452	0.7077	2.5536	0.9773		
	310	209.36	-0.003	0.9989	0.8848	-2.2557	0.9989	$0.9\pm0.203$	278.37
	320	179.54	-0.014	0.9449	1.1992	-2.1346	0.9449		
	330	230.27	-0.047	0.9936	0.9139	-1.2060	0.9936		

Table 5 Furamelers for the experimen	Table 3	meters for the experime.	ıtal	data
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\*Reaction order. \*\*Activation Energy

The main difference between the thermal and catalytic cracking is the reaction yield was obtained as for thermal cracking, 63% for the Al / Si, 86% to the Al / Si 1% Zn and 89% the catalyst with 2% Zn, 90% yield.



Figure 5 Conversion of the waste motor oil as function of the temperature for the different reactions

#### Conclusions

In this investigation the thermal and catalytic cracking reaction of waste motor oil was studied. The use of the catalyst enables high conversions with moderate reaction conditions, that is, the cracking temperature is reduced in a 350°C in the heat treatment at 330°C in the catalytic process reaching a high conversion and selectivity. The final product of the different processes of thermal and catalytic cracking meets all necessary requirements for diesel # 2.

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# BIFURCATIONAL PARAMETRIC SIMPLIFICATION IN CHEMICAL KINETICS

Gregory Yablonsky<sup>1</sup>, Vladimir Gol'dshtein<sup>2</sup>, Natalia.Krapivnik<sup>2</sup> <sup>1</sup>Parks College of Engineering, Aviation and Technology, Saint Louis University, St. Louis MO 63103, USA <sup>2</sup> Department of Mathematics, Ben-Gurion University, P.O.B., 653, Beer-Sheva, 84105, Israel.

## Abstract

Phenomenon of bifurcational parametric simplification has been distinguished for dynamic systems and has been applied to chemical kinetics models. The theory of bifurcations has been used for justification of this phenomenon. A method of 'slow-fast' dynamics, in particular a coordinate-free version of the singular perturbation theory, was presented as a technical tool for a rigorous evaluation of asymptotic analytic expressions that combine different kinetic parameters. The developed concept has been illustrated by the example taken from kinetics of heterogeneous catalysis (Langmuir-Hinshelwood mechanism), and analytical expression for reaction rates at ignition and extinction points have been re-examined. For this model, a point of the 'maximal complexity' that merges ignition and extension points has been found and analyzed.

## Keywords

Bifurcational simplification, ignition, extinction, Langmuir-Hinshelwood mechanism

A concept of 'critical simplification' was proposed by Yablonsky and Lazman in 1996 [1] for oxidation of carbon monoxide over a platinum catalyst using the Langmuir- Hinshelwood mechanism, see [2] and [3] as well. The main observation was a dramatic simplification of the corresponding kinetic model at ignition and extinction points. Critical simplification is very different from typical scenarios of simplification well known in chemical kinetics, i.e. limiting, pseudoequilibrium or pseudo-steady-state behavior.

In this paper it is shown that the critical simplification is a manifestation of much more general phenomenon which we call a bifurcational parametric simplification.

Roughly speaking a mathematical bifurcation is a qualitative change of an asymptotic dynamics due a smooth and slow changes of parameters. A typical example is the famous Hopf bifurcation that describes a change from an equilibrium to oscillations. These qualitative changes can be continuous and slow (bifurcation theory) but can be also fast and even very fast (catastrophe theory). By E.C. Zeeman "the world is full of sudden transformations and unpredictable divergences" that are subjects of the catastrophe theory.

Any bifurcation produces a dependence between system parameters and this is a mathematical explanation and/or a justification of the "parametric simplification". It leads us to a conjecture that "maximal bifurcational parametric simplification" corresponds to the "maximal bifurcation complexity".

It is an open problem what is the "maximal bifurcation complexity" in the context of kinetic models. We hope that a study of benchmark models can lead us to a better understanding of this phenomenon.

This conjecture can have practical application for experimental study, because a number of independent parameters at points of "maximal bifurcation complexity" is minimal. Other parameters can be evaluated analytically or numerically.

We illustrate this method on the case of multiplicity of steady states. In this case, a machinery of algebraic geometry and singularity theory can be relevant.

Our analysis is applied to the dynamic model which corresponds to the Langmuir mechanism of catalytic oxidation reaction. An analytical approach is based on a coordinate-free version of the method of invariant manifolds proposed recently [4]. As a result, different scenarios of the bifurcational parametric simplification are described in terms 'reaction rate vs substance concentration', and a physico-chemical interpretation of monoparametric dependences is given.

The Langmuir mechanism of catalytic CO oxidation over Pt is presented as a set of steps

(1)  $O_2 + 2Z \longrightarrow 2 OZ$ (2)  $CO + Z \longleftrightarrow COZ$ (3)  $OZ + COZ \longrightarrow CO_2 + 2Z$  $2 \quad CO + O_2 \overleftrightarrow 2 CO_2$ ,

where Z, OZ and COZ are an empty catalytic site, adsorbed oxygen and adsorbed CO, respectively.

The steady-state model for this mechanism is

$$\frac{d\theta_{\rm OZ}}{dt} = 2k_1^+ p_{\rm O_2}\theta_{\rm Z}^2 - k_3^+\theta_{\rm OZ}\theta_{\rm COZ} = 0 \tag{1}$$

$$\frac{d\theta_{\text{COZ}}}{dt} = k_2^+ p_{\text{CO}} \theta_{\text{Z}} - k_2^- \theta_{\text{COZ}} - k_3^+ \theta_{\text{OZ}} \theta_{\text{COZ}} = 0 \quad (2)$$

where  $\theta_Z$ ,  $\theta_{OZ}$ ,  $\theta_{COZ}$  are surface concentrations of Z. OZ and COZ, respectively;  $k_1^{+}$ ,  $k_2^{+}$ ,  $k_2^{-}$ , and  $k_3^{+}$ , are rate coefficients of corresponding reactions.

The partial pressures  $p_{O_2}$  and  $p_{CO}$  are considered to be parameters of our model with  $p_{O_2}$  constant and  $p_{O_2} >> p_{CO}$ , while the steady-state rate dependence on the gas-phase composition is assumed to be monoparameteric:  $r = k_3^+ \theta_{OZ} \theta_{COZ} = f(p_{CO})$ .



Partial pressure of CO

Figure 1. Multiple steady states; reaction rate versus  $P_{CO}$ ; irreversible adsorption of  $O_2$  and reversible adsorption of CO.

At sufficiently high values of the rate coefficient  $k_3^+$ , analytical solutions for three branches corresponding to the different kinetic regimes can be obtained:

$$r_{\rm CO_2} = \begin{cases} r_{\rm I} = \left(k_2^+ p_{\rm CO}\right)^2 / 2k_1^+ p_{\rm O_2} & \text{(branch I)} \\ r_{\rm II} = k_2^- \left(\sqrt{H} + \sqrt{H-1}\right)^2 & \text{(branch II)} \\ r_{\rm III} = k_2^- \left(\sqrt{H} - \sqrt{H-9^2}\right)^2, & \text{(branch III)} \end{cases}$$
(3)

where

$$H = \frac{\left(k_2^+ p_{\rm CO} + k_2^-\right)^2}{8k_2^- k_1^+ p_{\rm O_2}} \tag{4}$$

The first (upper) and third (lower) branches are stable, the second is unstable.

Figure 1 presents this phenomenon qualitatively. Point A and C are the ignition and extinction points with steady state rates  $r_{ign}$  and  $r_{ext.}$ , respectively,

It was shown analytically that at the extinction point C,

$$r_{\text{ext.}} = r_{\text{c}} = 2k_1^+ p_{\text{O}_2} = k_2^+ p_{\text{CO,C}}$$
 (5)

where  $p_{co,c}$  is the critical pressure of CO at which extinction is observed.

Thus, the steady-state reaction rate at the extinction point is determined by the kinetic characteristics of the adsorption step only.

At the ignition point A, which is characterized by

H = 1, and

$$r_{\rm II} = r_{\rm III} = r_{\rm A} = r_{\rm ign} = k_2^-$$
 (6)

There are two external parameters which are maintained constant during this experiment, the partial pressure of oxygen and temperature. Coefficients of adsorption for both oxygen and CO depend on the temperature insignificantly. In accordance with (5) and (6), the rate at extinction point will be a function of only partial pressure of oxygen only, and the rate at ignition point will be a function of only temperature. At the bifurcation point of the 'maximal complexity' in which the ignition point and extinction are merged

 $k_{2-} = k_2 p_{co} = 2k_1 p_{O2}$  (7) and  $K_{2,eq} p_{CO} = 1$  (8), where  $K_{2,eq}$  is the equilibrium constant of CO adsorption. In this case the point of "maximal bifurcation complexity is a cusp point in terms of the bifurcation theory. It depends on vanishing of two bifurcation parameters. Number of bifurcation parameters depends on "bifurcation complexity".

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# **ON THE REACTION OF RO2 RADICALS WITH OH RADICALS**

Christa Fittschen University of Lille – Villeneuve d'Ascq F-59655 Villeneuve d'Ascq, France

Keywords

Peroxy radicals, remote atmosphere

Peroxy radicals ( $RO_2$ ) play a key role in atmospheric chemistry. In polluted environments, they react predominantly with NO, leading to formation of  $NO_2$  which through subsequent photolysis leads to formation of  $O_3$ .

At low NOx concentrations such as in the remote continental or marine boundary layer or the background troposphere, the lifetime of  $RO_2$  radicals increases and other reaction pathways become competitive for peroxy radicals. Atmospheric chemistry models currently consider self- and cross reactions with other  $RO_2$  radicals or with  $HO_2$  radicals as major fate for  $RO_2$  radicals under these conditions, in the example of  $CH_3O_2$ :

$$CH_3O_2 + CH_3O_2 \longrightarrow 2 CH_3O + O_2$$
 (R1a)

 $\rightarrow$  CH<sub>2</sub>O + CH<sub>3</sub>OH + O<sub>2</sub> (R1b)

$$CH_3O_2 + HO_2 \longrightarrow CH_3O_2H + O_2$$
(R2)

Currently, the reaction of RO2 radicals with OH radicals

$$RO_2 + OH \rightarrow products$$
 (R3)

is not considered in models such as MCM, even though recent work has shown for  $CH_3O_2$  [1,2] and for  $C_2H_5O_2$  radicals [3] that this reaction is fast enough to compete with (R1) and (R2). In order to evaluate the ultimate impact of this reaction on the composition of the atmosphere, the major question is: what are the products of this reaction? Currently, experiments are being carried out to answer this question and the state of knowledge will be presented at the conference. Also, model calculations will be presented to illustrate the impact of including this reaction into models onto the chemistry of the atmosphere.

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# THERMOCHEMICAL CLOSURE OF UPTAKE AND EVAPORATION KINETICS OF H<sub>2</sub>O, HNO<sub>3</sub> AND HCl ON ATMOSPHERIC ICES IN THE RANGE 170 TO 210 K

Riccardo Iannarelli and Michel J. Rossi\* Paul Scherrer Institute (PSI), ETH Domain Villigen PSI, CH-5232, Switzerland

### Abstract

We present the fundamental heterogeneous kinetics of interaction of atmospherically relevant gases such as H<sub>2</sub>O, HNO<sub>3</sub> and HCl on solid ices composed of pure H<sub>2</sub>O, H<sub>2</sub>O/HNO<sub>3</sub> ( $\alpha$ -,  $\beta$ -NAT, NAD) and H<sub>2</sub>O/HCl (HCl•6H<sub>2</sub>O) in the atmospherically relevant range 170 to 210 K. Both steady-state uptake and pulsed gas admission experiments have been performed using 1-2 µm thick ice substrates as surrogates of atmospheric particles using a multidiagnostic stirred flow reactor (SFR) equipped with both gas-phase (residual gas MS) as well as condensed phase (FTIR spectrometry in transmission) detection. The kinetic data have been expressed as the mass accommodation coefficient  $\alpha$  for adsorption and the rate of evaporation ( $R_{ev}$ /molecule cm<sup>-3</sup>s<sup>-1</sup>) or the evaporative flux J<sub>ev</sub> (molecule cm<sup>-2</sup>s<sup>-1</sup>) for desorption of the atmospheric gas probes. The ratio of the first-order adsorption to the zero-order desorption rate constant yields the vapor pressure of the corresponding gas over the frozen solid and is represented in terms of a phase diagram. This thermochemical constraint is compared to literature values and ensures that the kinetic results are obeying to detailed balancing.

#### Keywords

Heterogeneous Kinetics, Mass Accommodation Coefficient, Rate of Evaporation, Thermochemistry, Vapor Pressure, Atmospheric Ice Particles, Nitric Acid Dihydrate (NAD),  $\alpha$ -,  $\beta$ -Nitric Acid Trihydrate (NAT)

## Introduction

Heterogeneous chemistry on ice surfaces taking place on ice clouds in the Upper Troposphere (UT) or on Polar Stratospheric Clouds (PSC's) in the Lower Stratosphere (LS) have been recognized to be the seat of gas-surface interfacial (heterogeneous) chemical processes. These deplete ozone during both the Antarctic and Arctic Spring after chlorinecontaining reservoir (stable) gases have been converted into a photolabile form in so-called chlorine-activation processes during the long winter season (Solomon, 1990). PSC's form during the winter and are made up of either pure ice (PSC type II) or nitric acid trihydrate (HNO<sub>3</sub>•3H<sub>2</sub>O, PSC type Ia). Their presence during the winter enables heterogeneous chemical reactions such as displayed in Eq. (1):

$$ClONO_2(g) + HCl(s) \rightarrow Cl_2(g) + HNO_3(s)$$
 (1)

In which the chlorine (unreactive) reservoir  $ClONO_2$ reacts with HCl at a rate faster by orders of magnitude compared to the corresponding gas phase reaction. The principal reason for this rate enhancement is the fact that the reaction mechanism changes from the interaction of two stable closed shell molecules in the gas phase to essentially the reaction of a chloride anion • <u>michel.rossi@psi.ch</u> To whom all correspondence should be addressed

with the reservoir chlorine nitrate. Pure H<sub>2</sub>O ice as well as HNO<sub>3</sub> and HCl-containing ices support spontaneous ionic dissociation of HCl into H<sub>3</sub>O<sup>+</sup>•••Cl<sup>-</sup>(ads), hence the importance to explore the chemical reactivity of the condensed phase in terms of fundamental processes such as mass accommodation (adsorption)  $\alpha$  and molecular evaporation R<sub>ev</sub> of relevant atmospheric trace gases such as HNO<sub>3</sub> and HCl including H<sub>2</sub>O. Typical H<sub>2</sub>O, HNO<sub>3</sub> and HCl concentrations in the UT/LS are 5 ppm, 10 and 2 ppb, respectively, in the broad temperature range 185 to 210 K (excluding winter). The rising sun in the polar spring will efficiently photodissociate Cl<sub>2</sub> into 2Cl<sup>•</sup> that are chain carriers in the catalytic destruction of O<sub>3</sub> with typical chain lengths of 10<sup>4</sup> – 10<sup>5</sup> as displayed in Eq. (2):

$$\operatorname{Cl}^{\bullet}(g) + \operatorname{O}_3 \twoheadrightarrow \operatorname{ClO}^{\bullet}(g) + \operatorname{O}_2$$
 (2)

We report on (1) the growth of HNO<sub>3</sub>- as well as HClcontaining thin ice films of typically 1-2  $\mu$ m thickness that we take as surrogates of atmospheric ice particles and observe the growth of crystalline Nitric Acid Trihydrate (HNO<sub>3</sub>•3H<sub>2</sub>O, both metastable  $\alpha$ - and stable  $\beta$ -NAT) and metastable Nitric Acid Dihydrate (HNO<sub>3</sub>•2H<sub>2</sub>O, NAD) phases, respectively. Once we have obtained the atmospherically relevant phases as thin solid ice films at low temperatures in the range 170 to 180 K we probe (2) the interfacial (gas-surface) kinetics of H<sub>2</sub>O, HNO<sub>3</sub> and HCl in terms of massaccommodation coefficient  $\alpha$  and the corresponding rate of evaporation R<sub>ev</sub> in a systematic way as a function of external parameters such temperature of the condensed phase, partial pressure of the probe gas, dose, etc.

## **Experimental Apparatus**

multidiagnostic The experiments are performed in a Stirred Flow Reactor (SFR) displayed in Figure 1. It is equipped with residual gas electronimpact quadrupole mass spectrometry, high-sensitivity capacitance manometry and transmission FTIR spectroscopy at 4 cm<sup>-1</sup> resolution in order to monitor both gas as well as condensed phases under identical experimental conditions. Several series of independent uptake measurements, both steady-state and pulsed (transient supersaturation experiments), are performed in order to separate both the adsorption and desorption rate constants leading to mass accommodation coefficients ( $\alpha$ ) and zero-order rates or fluxes of evaporation (Rev,, Jev) for both atmospheric gases, H2O and HNO<sub>3</sub>. The cryostat housed in the stainless-steel vessel operating as SFR has been described in detail before (Iannarelli, 2014; Iannarelli and Rossi, 2014). Briefly, the special feature of the SFR is its thermally insulated liquid N<sub>2</sub>-cooled cryostat installed on the cylinder axis of the reaction vessel that presents a temperature-controlled, usually cold, Si-window of 1 cm<sup>2</sup> area to the flowing gases. It serves as a support to the vapor-condensed thin solid films of ices in order to enable transmission spectroscopy in the mid-IR (4000 to 700 cm<sup>-1</sup>). Most importantly, all cryogenic parts of the cryostat except the Si-window are thermally insulated by a vacuum-tight sleeve made of FEP Teflon such that the gas only interacts with the cold Siwindow whose temperature is measured using two type T (Copper-Constantan) thermocouples. Because  $H_2O$ , HNO<sub>3</sub> and HCl are gases that "stick" to the stainless steel walls held at 315 K the Langmuir adsorption isotherm was measured at 315 K enabling the correction of the number of molecules adsorbed on the stainless steel walls as a function of its partial pressure when establishing mass balances. These two features, namely controlling the interaction of the flowing gases on a well-defined area and correcting for walladsorption of the gases proved essential in order to obtain quantitative results under conditions of mass balance.

## **Results and Discussion**

Thermochemical closure (detailed balancing) has been achieved in the HNO<sub>3</sub>/H<sub>2</sub>O system by taking the ratio  $R_{ev}/\alpha \cdot \omega$  resulting in the corresponding vapor pressure P of both H<sub>2</sub>O and HNO<sub>3</sub> at a given temperature, with  $\omega$  being the known (calculated) gaswall collision frequency and the product  $\alpha \cdot \omega$ 

corresponding to the first-order adsorption rate constant  $k_{het}$ . The calculated vapor pressures agree with known literature values from the corresponding phase diagrams and therefore represent a constraint on the kinetics of both adsorption and evaporation, the latter of which have been measured for the first time as there are no values for  $R_{ev}$  in the literature, neither for the crystalline HNO<sub>3</sub>/H<sub>2</sub>O substrates nor for HCl. For pure ice substrates there are literature values available.



Figure 1. The Multidiagnostic Stirred Flow Reactor (SFR).



Figure 2. HNO<sub>3</sub> Dosing of pure ice and concomitant generation of an α-NAT/ice composite ice film.


Figure 3. Typical kinetic data set for β-NAT with thermodynamic constraint. Transient (full symbols) and steady-state results are different.

The interfacial kinetics of trace gas-condensed phase will be presented as a function of temperature, and the thermodynamics (equilibrium vapor pressures as a function of substrate temperature) will be discussed in the framework of existing phase diagrams. In addition, the kinetics and thermodynamics of H<sub>2</sub>O, HNO<sub>3</sub> and HCl interacting with H<sub>2</sub>O ice will be compared to the analogous HCl/H2O system that we have recently the measured using identical experimental methodology (Iannarelli and Rossi, 2014). The lower panel of Figure 2 presents a time series of HNO<sub>3</sub> dosing on pure ice leading to  $\alpha$ -NAT whereas the upper panel displays the corresponding changes in the IR absorption spectrum as a function of time with a sequence of color-coded mid-IR spectra of our multidiagnostic experiment. The different contributions to the HNO<sub>3</sub> signal are labelled in terms of the absolute number N of molecules in question, namely the number of HNO<sub>3</sub> flowing in (N<sub>in</sub>), escaping the SFR across the orifice (Nesc), and lost to the vessel walls by adsorption  $(N_{ads,w})$  with  $N_{loss}$  being the sum of  $N_{esc}$  and  $N_{ads,w}$ . The hatched area represents the cumulative number of HNO<sub>3</sub> adsorbed on the ice substrate which is used in mass balance considerations together with data on H<sub>2</sub>O (not shown). The  $\beta$ -NAT phase has been grown through thermal rearrangement of  $\alpha$ -NAT starting at 185 K. Some of the main results will now briefly be



Figure 4. Typical kinetic data set for  $\beta$ -NAT including detailed balancing for HNO<sub>3</sub> and HCl, but not for H<sub>2</sub>O.

presented and discussed. Rev of H2O is generally smaller by an order of magnitude for both NAT and NAD compared to pure H<sub>2</sub>O ice in the stated T-range. For HNO<sub>3</sub> the differences amount to three to four orders of magnitude coupled to a higher activation energy than for H<sub>2</sub>O. Figure 3b displays this fact and shows that the relevant kinetic parameter is the rate of evaporation of HNO<sub>3</sub> that is responsible for the small vapor pressure above  $\beta$ -NAT. Similar results have been obtained for  $\alpha$ -NAT (not shown). This situation prevails despite the fact that  $\alpha$ (HNO<sub>3</sub>) is larger by an order of magnitude compared to H<sub>2</sub>O (Figure 3c). This has important consequences on the evaporative lifetime of atmospheric ice particles provided these have compositions similar to the present laboratory work. The kinetic data show that pure ice, once contaminated by HNO<sub>3</sub> and HCl (Iannarelli and Rossi, 2014; Iannarelli 2014) will remain so until the end of the lifetime of the ice particle. The only way to get rid of the contaminant is to completely evaporate the ice particle. This fact has ramifications for atmospheric ice chemistry because it is expected that most ice particles including PSC type II will be contaminated by atmospheric trace gases in view of the large measured accommodation coefficients. In summary, it is difficult to imagine the presence of "pure" ice particles in the atmosphere. A relevant detail displayed by the data of Figure 3 is the fact the kinetics of H<sub>2</sub>O adsorption on  $\alpha$ -NAT and  $\beta$ -NAT (Figure 3c) are subject to partial saturation on the solid ice substrate because  $\alpha$  is smaller when pulsed dosing is used compared to the steady-state flow technique. Pulsed dosing keeps the H<sub>2</sub>O dose to a minimum when small dose pulses (short opening times of the solenoid valve) are used. Unfortunately, this difference has not been observed for HNO<sub>3</sub> because no pulsed dosing experiments could be performed for HNO<sub>3</sub>. However, we know from NAT and NAD growth experiments on pure ice that growth slows down with constant HNO<sub>3</sub> dosing as it becomes harder for HNO<sub>3</sub> to diffuse across the already existing NAT coating in order to build up additional NAT at the "pure" ice-NAT solid interface.

In contrast to similar amorphous phases the values of  $\alpha$  pertaining to crystalline  $\alpha$ -,  $\beta$ -NAT and NAD are scattered and lie within a band of approximately a factor of 20 as displayed in Figure 3c. This scatter in  $\alpha$  is not due to random noise upon separation of the primary uptake data into  $\alpha$  and k<sub>het</sub> because corresponding data of  $\alpha$ (HCl) on an amorphous H<sub>2</sub>O/HCl solid show considerably less scatter (less than 50%). The scatter on a crystalline phase has to do with the stochastic nature of the crystallization process yielding a surface whose composition and crystal facets change from one sample to the next. However, this scatter also applies to R<sub>ev</sub> resulting in significantly less scatter for the equilibrium vapor pressure of both H<sub>2</sub>O and HNO<sub>3</sub> because of the compensating effect.

Figure 4 displays the interaction of HCl on  $\beta$ -NAT as a function of temperature. The kinetic data have been obtained by assuming that the accommodation coefficient of HNO<sub>3</sub> is identical to the one for  $\beta$ -NAT in the absence of HCl:  $\alpha$ (HNO<sub>3</sub>) displayed in Fig 4c is identical to Fig 3c. As expected the vapor pressure of HCl over  $\beta$ -NAT is larger than for HNO<sub>3</sub> in agreement with the corresponding phase diagrams (not shown). However, the reason seems to lie in the  $\alpha$ (HCl) value that is significantly lower than for HNO<sub>3</sub> in view of similar values of Rev(HCl) compared to Rev(HNO<sub>3</sub>) in the range 190 to 200 K as displayed in Figure 4b.  $R_{ev}(HNO_3)$  is identical to pure  $\beta$ -NAT, perhaps not unexpected. The present conclusions are at variance with a comparable study albeit for a slightly higher temperature range (Hynes et al. 2002).

Both metastable HNO<sub>3</sub> hydrates on ice ( $\alpha$ -NAT, NAD) grow spontaneously without having a nucleation barrier on a pure ice film in contrast to crystalline HCl hexa- and trihydrates. The acidic trace gases HNO<sub>3</sub> and HCl as well as H<sub>2</sub>O have large accommodation coefficients, but the growth of a new ice phase seems to depend on the diffusion rate of the trace gas across the newly-forming ice phase. In this regard it is expected that HCl diffuses faster than both HNO<sub>3</sub> and H<sub>2</sub>O because the former has can only form a single hydrogen bond whereas the latter both can form two. Therefore, we expect that the kinetics of HCl is less prone to saturation which is indeed the case: no saturation effects have been observed for HCl. As a "byproduct" we have measured the absolute IR 2.0x10<sup>-18</sup> α-NA 1.6 NAD σ [cm<sup>2</sup> · molec β-ΝΑΤ 1.2 0.8 0.4 0.0 2.0x10<sup>-18</sup> 1.6 σ [cm<sup>2</sup> · molec 1.2 0.8 0.4 0.0 2.0x10<sup>-18</sup> 1.6 o [cm<sup>2</sup> · molec<sup>-1</sup> 1.2 0.8 0.4 0.0 4000 3500 3000 2500 2000 1500 1000 Wavenumber [cm<sup>-1</sup>]

Figure 5. Cross sections of  $\alpha$ -NAT, NAD and  $\beta$ -NAT in the temperature range 168 to 200K.

cross sections  $\sigma(\lambda)$  in the range 4000-700 cm<sup>-1</sup> of  $\alpha$ -,  $\beta$ -NAT and NAD ices using the mass balance information on H<sub>2</sub>O and HNO<sub>3</sub>. Despite previous work on optical constants of these ices the present value of  $\sigma(\lambda)$  is the first report in the literature which should prove valuable in remote sensing applications.

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# DIRECT KINETIC MEASUREMENTS OF THE REACTIONS OF THE SIMPLEST CRIEGEE INTERMEDIATE CH<sub>2</sub>OO WITH ALKENES AND CARBONYL COMPOUNDS

Rehab M. I. Elsamra,<sup>†</sup>,<sup>‡</sup> Zachary J. Buras,<sup>†</sup> Amrit Jalan,<sup>†</sup>a Joshua E. Middaugh,<sup>†</sup>b and William H. Green<sup>†</sup>,\* <sup>†</sup>Massachusetts Institute of Technology, Cambridge, MA 02139, USA <sup>‡</sup>Alexandria University, 21321 Alexandria, Egypt

a) Present Address: ExxonMobil Research & Engineering, Annandale, NJ, USAb) Present Address: Air Products and Chemicals, Inc., Allentown, PA, USA

#### Abstract

The *T*-dependence of the reactions of the simplest Criegee Intermediate with C2–C4 alkenes and carbonyl compounds has been experimentally determined using Laser flash photolysis coupled with uv absorption technique. 375nm photons were used to probe the recently measured  $B^1A' \leftarrow X^1A'$ transition in CH<sub>2</sub>OO. The measured activation energy (298–494 K) for CH<sub>2</sub>OO + alkenes is  $E_a \approx 3500 \pm 1000$  J mol<sup>-1</sup> for all alkyl substituted alkenes while it is approximately double at  $E_a = 7000 \pm 900$  J mol<sup>-1</sup> for unsubstituted ethene. The activation energy for the reactions with the carbonyl compounds, CH<sub>3</sub>COCH<sub>3</sub> and CH<sub>3</sub>CHO, is negative at  $E_a \approx -1100 \pm 50$  J mol<sup>-1</sup>. The measured Arrhenius pre-exponential factor (*A*) for the reactions with alkenes is approximately similar to that measured for the reaction with carbonyl compounds, implying that the difference in their reactivity towards CH<sub>2</sub>OO is due to the depth of the submerged transition state. Over the studied temperature range, rate coefficients for CH<sub>2</sub>OO + carbonyl compounds are two orders of magnitude higher than with alkenes. Using the rate constants measured here, we estimate that, reactions with alkenes or carbonyl compounds do not represent a significant sink of CH<sub>2</sub>OO but could be important in systems with high concentrations of carbonyl or C=C double bonds, e.g. the ozone-driven degradation of some polymers.

Keywords

Criegee intermediate, Alkenes, carbonyl compounds, uv absorption, absolute rate constants.

#### Introduction

Criegee Intermediates (CI) were postulated many years ago as important biradicals in atmospheric alkene ozonolysis (Criegee, et al., 1949) where they are likely to be formed with high internal energy and can initiate tropospheric oxidation reactions (Vereecken, et al., 2012). They also impact the atmospheric budgets of SO2 (Cox, et al., 1972) and NO<sub>X</sub> (Welz, et al., 2012 and Vereecken, et al., 2012) and are linked to the formation of H<sub>2</sub>SO<sub>4</sub> (Mauldin, et al., 2012). Direct kinetic measurements of the reactions of CI with neutral atmospheric molecules were only accessible recently, after Welz et al. demonstrated an efficient route for the formation of the simplest CI (CH<sub>2</sub>OO) through the reaction of  $CH_2I + O_2$ . The rate of the reactions of CH<sub>2</sub>OO with alkenes is of great interest as CH<sub>2</sub>OO intermediates are commonly formed by reactions of ozone with alkenes. Reactions with carbonyl compounds have received special attention as the highly exothermic and barrierless cycloaddition of CI to the C=O bond makes them efficient CI scavengers. In the present work we report the temperature dependent rate

coefficients for reactions of CH<sub>2</sub>OO with C2-C4 alkenes (Buras, et al., 2014) and with CH<sub>3</sub>COCH<sub>3</sub> and CH<sub>3</sub>CHO. The results of the experiments enable us to compare between the addition of CH<sub>2</sub>OO on the C=O in CH<sub>3</sub>CHO and CH<sub>3</sub>COCH<sub>3</sub> and on C=C in alkenes. Furthermore, the products of the reaction CH<sub>2</sub>OO + CH<sub>3</sub>COCH<sub>3</sub> were measured at 10, 25 and 50 Torr by Photo-Ionization Time-of-Flight Mass Spectrometry (PI TOF-MS) using 10.5 eV photons and the effect of pressure was tested for all reactions between 10 and 50 Torr.

To whom all correspondence should be addressed

## Experimental

The laser flash photolysis/ Herriot multiple passes uv absorption apparatus used in this study is described by (Ismail, et al., 2009). This apparatus is coupled with a PI TOF-MS with supersonic molecular beam sampling from the center of the reactor. Detailed descriptions of the two techniques are available in the published MIT, Ph.D. Thesis (Middaugh, et al., 2014) and only the essential details are included here. The reactor is 86 cm long, 6 cm in diameter and resistively heated by four heaters wrapped along the length of the reactor to create a uniform temperature profile. The heaters enable the gas mixture to be heated up to 700 K, though in the present work, measurements were limited to 500 K to avoid secondary chemistry that could arise from the thermal decomposition of CH<sub>2</sub>OO at high temperatures. The internal pressure of the reactor was monitored by a capacitance manometer and controlled via an automated butterfly valve. CH2OO radicals were generated by the photolysis of CH<sub>2</sub>I<sub>2</sub> in the presence of O<sub>2</sub>, a method demonstrated by Welz et al., In the present experiments, in order to minimize the possibility of CH<sub>2</sub> formation (via a single-photon process (Baughcum, et al., 1980)) or photolytic fragmentation of either CH<sub>3</sub>CHO or CH<sub>3</sub>COCH<sub>3</sub>, the third harmonic output of a Nd:YAG laser (355 nm) operated at a repetition rate of 2 Hz was used to photolyze CH<sub>2</sub>I<sub>2</sub>. The frequency-doubled output of a Ti:Sapphire laser (80 MHz pulsed laser with 1.2 ps Full Width at Half Maximum, FWHM, wide pulses) was used to generate the ultraviolet probe beam, 375 nm and the fundamental wavelength was measured before each experiment using a recently calibrated Ocean Optics USB2000 spectrometer. Multiple-pass probe laser path lengths were in the range of 10-15 m. Ultraviolet absorbance traces were averaged over 500 acquisitions. Infrared absorption of the co-product I atoms atomic transition (F= 3  ${}^{2}P_{1/2} \leftarrow$  F=4  ${}^{2}P_{3/2}$ ) (Ha, et al., 1995) was used to determine the concentration of CH<sub>2</sub>OO radicals.

Helium was used as a balance gas. The flow of this gas was varied to adjust the total gas mixture flow and maintain the same number of photolysis flashes per refresh. All experiments were operated at one flash per refresh to avoid secondary chemistry.

The relative time-dependent product concentrations for the reaction of  $CH_2OO$  with  $CH_3COCH_3$  were determined using the PI TOF-MS method. A small amount of the reactive gas mixture was continuously sampled *via* a small pinhole at the tip of a cone that juts slightly into cross section of the photolysis beam at the center of the reaction cell. The sampled gas was

supersonically expanded, and the center of the resultant free jet was passed through a Beam Dynamics skimmer to form a collimated molecular beam. The gas in the molecular beam was effectively "frozen" in composition by cooling while in transit to the ionization region of the PI TOF-MS, where it was photo-ionized using 118.2 nm (10.487 eV) light. The relative abundance of ions at different mass-to-charge ratios (m/z) were analyzed using a Kore Time-of-Flight mass spectrometer and detected using the Kore-supplied discrete dynode electron multiplier detector and analog pre-amplifier. The correspondence between time-of-flight and m/z was determined by calibration with a mixture of known stable species. P-dependent experiments were conducted for all the titled reactions between 10 to 50 Torr He.

#### **Results and Discussion**

Once generated, CH<sub>2</sub>OO radicals undergo reactions with the co-reactants CH<sub>3</sub>COCH<sub>3</sub>, CH<sub>3</sub>CHO or C2-C4 alkenes ( $k_2$ ), and removed from the center of the reactor by other process. A full scheme for the possible removal processes of CH<sub>2</sub>OO in our system is as follows:

$$\begin{array}{c} \mathrm{CH}_{2}\mathrm{I}_{2} \xrightarrow{355 \text{ nm}} \mathrm{CH}_{2}\mathrm{I} + \mathrm{I} \\ \mathrm{CH}_{2}\mathrm{I} + \mathrm{O}_{2} \xrightarrow{k_{1}} \mathrm{CH}_{2}\mathrm{OO} + \mathrm{I} \\ \mathrm{CH}_{2}\mathrm{OO} + (\mathrm{C}{=}\mathrm{O}/\mathrm{C}{=}\mathrm{C}) \xrightarrow{k_{2}} \mathrm{Products} \\ \mathrm{CH}_{2}\mathrm{OO} + \mathrm{CH}_{2}\mathrm{OO} \xrightarrow{k_{\mathrm{self}}} \mathrm{Products} \\ \mathrm{CH}_{2}\mathrm{OO} + \mathrm{I} \xrightarrow{k_{\mathrm{CH2OO}_{1}}} \mathrm{Products} \\ \mathrm{CH}_{2}\mathrm{OO} \xrightarrow{k_{3}} \mathrm{Products} \\ \mathrm{CH}_{2}\mathrm{OO} \xrightarrow{k_{3}} \mathrm{Products} \end{array}$$

Reactions are carried out under pseudo first order conditions, where the co-reactant, is put in excess over the initial concentration of  $CH_2OO$ . A single exponential function was able to fit the absorption traces well at all temperatures less than 500 K as shown in figure 1. The resultant pseudo-first order rate coefficients are plotted as a function of the co-reactants concentrations at different temperatures, Figure 2.



Figure 1. Time resolved absorption signal of CH<sub>2</sub>OO probed by 375 nm photons at experimental conditions of  $[O_2] = 6 \times 10^{16}$  molecules cm<sup>-3</sup>,  $[CH_2I_2] = 1.4 \times 10^{14}$  molecules cm<sup>-3</sup> and  $[CH_3CHO] = 1.0 \times 10^{15}$ molecules cm<sup>-3</sup>. Signals represent three different temperatures at 25 Torr. The black dotted lines are single exponential fits. The reaction is fastest at low T.



Figure 2. Pseudo-first-order rate constant of  $CH_2OO$ as a function of  $[CH_3CHO]$  at T = 298 K (squares), 390 K (triangles) and 494 K (circles).



Figure3. Arrhenius plot of the experimentally determined rate constants for the  $CH_2OO + CH_3COCH_3$ ,  $CH_3CHO$ , and C2-C4 alkenes together with the best fit to k = Aexp(-E/RT), lines, and statistical and systematic errors. Note that the fit values of A (y-intercept) are all within the same order of magnitude.

Table 1: Arrhenius fits for the reactions with CH<sub>3</sub>COCH<sub>3</sub>, CH<sub>3</sub>CHO and C2-C4 alkenes at 25 Torr

	$A(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	E <sub>a</sub> (J mol <sup>-1</sup> )	$k_{298K}$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )
Ethene	$(11 \pm 3) \times 10^{-15}$	$\begin{array}{rrr} 7000 & \pm \\ 900 \end{array}$	$(0.7 \pm 0.1) \times 10^{-15}$
Propene	$(8 \pm 2) \times 10^{-15}$	$\begin{array}{rrr} 3700 & \pm \\ 600 \end{array}$	$(1.8 \pm 0.3) \times 10^{-15}$
Iso-butene	$(5 \pm 2) \times 10^{-15}$	$\begin{array}{rrr} 3400 & \pm \\ 1300 \end{array}$	$(1.4 \pm 0.3) \times 10^{-15}$
1-Butene	$(5\pm2) imes10^{-15}$	$3200 \pm 1400$	$(1.5 \pm 0.3) \times 10^{-15}$
2-Butene	$(2\pm1) imes10^{-15}$	$3500 \pm 1700$	$(0.7 \pm 0.2) \times 10^{-15}$
Acetone	$(7\pm1)\times10^{-15}$	$-1120 \pm 54$	$(2.9 \pm 0.6) \times 10^{-13}$
Acetaldehyde	$(3 \pm 0.2) \times 10^{-14}$	-1100 ± 35	$(1.2 \pm 0.2) \times 10^{-12}$

The T-dependence results are summarized in Figure 3 and Table 1. The measured activation energy (298-494 K) for the unsubstituted ethene is approximately double its value for all alkyl substituted alkenes. The activation energy for the reactions with the carbonyl compounds, CH<sub>3</sub>COCH<sub>3</sub> and CH<sub>3</sub>CHO, is negative at  $E_{\rm a} \approx -1100 \pm 50 \text{ J mol}^{-1}$ . Such negative temperature dependence is common for reactions that have a longrange attraction between the reactants and low reaction barriers (Clary, et al., 1990). When comparing the reactivity of CH<sub>3</sub>CHO and CH3COCH3 with our data for alkenes the differences are obvious. At room temperature, rate coefficients for CH<sub>2</sub>OO+carbonyl compounds were found to be two orders of magnitude higher than with alkenes. Considering that reactions of CH<sub>2</sub>OO with double bonds (Cremer, et al., 1993 and Nguyen, et al., 2007) is expected to proceed mainly via1,3 dipolar cycloaddition (Vereecken, et al., 2014), then the increase in the rate coefficients ingoing from alkenes to carbonyl compounds is likely to be due to the differences in the nature of the corresponding double bonds. The C=O bond is expected to be more reactive towards CH<sub>2</sub>OO on account of its higher dipolar character compared to the C=C bonds in The measured Arrhenius pre-exponential alkenes. factors (A) vary between  $(2 \pm 1) \times 10^{-15}$  and  $(11 \pm 3) \times$  $10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for the alkenes. Similar (A) factors are measured for the reaction with carbonyl compounds, implying that the difference in their reactivity towards CH<sub>2</sub>OO is due to the depth of the submerged transition state (Buras, et al., 2014).

Our MS experiments for the reaction CH<sub>2</sub>OO + CH<sub>3</sub>COCH<sub>3</sub> agree qualitatively with the previous results and conclusions of Taatjes et al., 2012. Firstly, the only products observed from the reaction are at m/z = 104 and m/z = 89 (they also did not go to high enough ionization energies to see formic acid). Furthermore, the MS signal at m/z =89 is about 5 times more intense than that of 104 amu species. Finally, the

fact that the relative ratio of m/z = 89 to 104 at different pressures appears constant within the uncertainty of our measurements, supports the hypothesis that the 89 amu species is derived from a 104 amu adduct.

Theoretical analysis by Amrit Jalan, suggests that the overall kinetics for the reaction of CH<sub>2</sub>OO + C=O are determined mainly by the tight 1,3-cycloaddition saddle point. Both high- and low-pressure ratecoefficients show negative temperature dependence although the experimentally determined slope is in much better agreement with the low-pressure estimates. Insignificant pressure dependence is observed for the titled reactions at 298 K over the pressure range 10 to 50 Torr He, and no pressure effect could be discerned at 444 K. These findings are supported by the theoretical calculations, which predict that the Pdependence is insensitive to the collision energy transfer parameter and that the variations of the overall rate coefficients for the reactions are negligible as a function of pressure in the pressure range of interest.

#### Conclusion

We have determined the temperature dependence of the rate constants,  $k_2$ , for the CH<sub>2</sub>OO + (C=C/C=O) reactions over the temperature range 298-500 K. The results show a factor of 4 decreases in the rate of the reaction of CH<sub>2</sub>OO with CH<sub>3</sub>COCH<sub>3</sub> than with CH<sub>3</sub>CHO over this temperature range. Reaction of CH<sub>2</sub>OO with alkenes is 1-4 orders of magnitude slower than its reaction with carbonyl compounds. Based on the experimental and theoretical data, the impact of C=O/C=C compounds on the concentration of CH<sub>2</sub>OO in the atmosphere is only expected to be significant in areas where the mole fraction of carbonyl/alkenes compounds is high.

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# YIELDS OF NITRIC ACID AND PEROXYNITROUS ACID PRODUCTS IN THE HO<sub>2</sub> + NO REACTION DETECTED BY BY CAVITY RINGDOWN SPECTROSCOPY

Laura A. Mertens<sup>1</sup>, Fred A. Winiberg<sup>2</sup>, Hannah M. Allen, Sandy Wong<sup>1</sup>, Stanley P. Sander<sup>\*2</sup> and Mitchio Okumura<sup>1\*</sup> <sup>1</sup>Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA USA

<sup>2</sup>NASA Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA USA

#### Abstract

The reaction of  $HO_2$  with NO is important in Earth's atmosphere, participating in free radical cycles that deplete ozone in the stratosphere and form ozone in the troposphere. Butkovskaya have a small but significant yield for nitric acid in measurements performed using a turbulent flow reactor and chemi-ionization detection. In this study, we examine this reaction and search for nitric acid and its isomer HOONO in the reaction of  $HO_2$  with NO using mid-infrared cavity ringdown spectroscopy of products in a slow flow reactor with pulsed laser photolysis initiation.

#### Keywords

Atmospheric Kinetics, Gas Phase, Cavity Ringdown Spectroscopy. Free Radicals, NOx and HOx

#### Introduction

The reaction of the hydroperoxyl radical  $\mbox{HO}_2$  with NO

$$HO_2 + NO \rightarrow OH + NO_2$$
 (2)

plays a key role in oxidation chemistry throughout the atmosphere, converting  $HO_2$  to the more reactive hydroxyl radical OH. This reaction has a significant effect on ozone depletion in the stratosphere, and photochemical smog formation and hydrocarbon oxidation in the troposphere. In the atmosphere, these radicals cycle through this reaction during their lifetime; thus, even a small yield of a chain termination channel could impact model predictions of ozone concentrations. Butkovskaya, LeBras and co-workers

have reported low ( $\leq 1\%$ ) but significant yields for the chain-terminating formation of nitric acid[Butkovskaya et al., 2005, 2007 and 2009]

$$HO_2 + NO + M \rightarrow HONO_2 + M$$
 (1)

using a turbulent flow reactor coupled with Chem-Ionization Mass Spectrometer (CIMS) detection. The reported yields are sufficient to have significant effects on predictions of atmospheric models.[Cariolle et al., 2008] Yet for the past decade, this important result has not been verified by other techniques.

We report an investigation of the nitric acid yield of this reaction in a time-resolved flow-cell experiment using Mid-IR cavity Ringdown Spectroscopy to detect products. Absolute product yields are determined from known band intensities, with sensitivities sufficient to test the previous results of Butkovskaya *et al.*  \*To whom all correspondence should be addressed

#### **Experimental Methods**

The apparatus has been described elsewhere by Mollner et al., 2010 and Sprague et al., 2013. Pulsed Laser Photoloysis (PLP) was used to initiate free radical chemistry at or below room temperature and pressures up to 700 torr, in buffer gas containing nitrogen, oxygen and carbon monoxide. Molecular chlorine was photolyzed at 351 nm in the presence of either methanol or formaldehyde to generate  $HO_2$ radicals.

We employed Mid-Infrared Cavity Ringdown Spectroscopy (CRDS) to detect the  $v_1$  spectrum of HONO<sub>2</sub>, as well as that of a less stable isomer, peroxy nitrous (HOONO).[Cariolle et al, 2008] Contributions from secondary reactions (especially the formation of nitric acid from the reaction of OH + NO<sub>2</sub>) can be assessed by detection of a number of secondary products. Wall reactions are minimized due to the short timescales (< 10 ms) of the experiments. Secondary products including HO2NO2 and HONO are detected as well.

Experiments were performed with high pressures of CO, which rapidly convert OH products back to HO<sub>2</sub> (via HOCO or  $H + O_2$ ). Spectroscopic detection of CO<sub>2</sub> allow us to directly determine the extent of OH recycling.

Our sensitivity allow us to determine nitric acid and HOONO yields on the order of 0.2%.

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# A kinetic study of the CH<sub>2</sub>OO Criegee intermediate unimolecular reaction and bimolecular reactions with CH<sub>2</sub>OO, SO<sub>2</sub> and halogenated carboxylic acids using cavity ring-down spectroscopy

Rabi Chhantyal-Pun<sup>\*</sup>, Anthony Davey, Lucy Blacker, Carl J. Percival, Dudley E. Shallcross and Andrew J. Orr-Ewing University of Bristol Bristol, BS8 1TS, UK

Keywords

Criegee Intermediate, CH<sub>2</sub>OO, SO<sub>2</sub>, halogenated carboxylic acids, cavity ring-down spectroscopy.

Criegee intermediates are important species formed during the ozonolysis of alkenes. Reaction of stabilized Criegee intermediates with various species like SO<sub>2</sub>, NO<sub>2</sub> and carboxylic acids may contribute significantly to tropospheric chemistry.<sup>1, 2</sup> Reaction of Criegee intermediates with anthropogenic chemicals like halogenated carboxylic acids, might be a significant sink for these otherwise stable species in the atmosphere.<sup>3</sup> In the laboratory, self-reaction can be an important loss pathway for Criegee intermediates and thus needs to be characterized to obtain accurate bimolecular reaction rate coefficients.<sup>4, 5</sup> Unimolecular reactions due to thermal decomposition or isomerization also need to be characterized to obtain accurate Criegee intermediate steady state concentrations under both atmospheric and laboratory conditions. Results from our recent time-resolved kinetic measurements obtained using cavity ring-down spectroscopy for various reactions of the simplest Criegee Intermediate, CH<sub>2</sub>OO, at 293 K and under low pressure (7 to 30 Torr) conditions will be presented.<sup>6</sup> The effect of these reactions in the atmospheric chemistry of SO<sub>2</sub> and halogenated carboxylic acids will be discussed.

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# REACTION KINETICS OF HOMOGENEOUS TRANSFORMATIONS OF GUAIACOL IN URBAN WET AEROSOL PARTICLES

A. Kroflič<sup>†,\*</sup>, M. Grilc<sup>‡</sup> and I. Grgić<sup>†</sup> <sup>†</sup>Analytical Chemistry Laboratory, National Institute of Chemistry <sup>‡</sup>Laboratory of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry *SI*-1001 Ljubljana, Slovenia

## Abstract

The tropospheric aqueous-phase aging of guaiacol (2-methoxyphenol, GUA), a lignocellulosic biomass burning pollutant, is addressed in this work. Pathways of GUA nitration in aqueous solution under atmospherically relevant conditions are proposed and discussed from a kinetic perspective. Beside reactions with nitrite radicals  $(NO_2^{+})$ , nitronium ion  $(NO_2^{+})$  is shown essential for appropriate description of experimental data by the model function. Its importance in the environment is assessed and ecological perspective underlined. In contrast to concentrations of radical species, which are governed by the interplay between diffusion-controlled reactions and are therefore mostly constant, concentrations of electrophiles are shown very much dependent on the ratio of nitrite-to-activated aromatics in aqueous solution. Consequently, higher-generation nitration products can be assumed in the absence of the primary aromatic pollutant under remote atmospheric conditions. Therefrom, the threat for remote biotopes, i.e. rain forests and oceans, is emphasized.

#### Keywords

Atmospheric aqueous-phase aging, Wet aerosols, Biomass-burning methoxyphenols.

<sup>\*</sup> To whom all correspondence should be addressed

## Introduction

Aromatic compounds contribute significantly to the world budget of atmospheric pollutants. They compose up to 50% of the non-methane hydrocarbon mass in urban air and many of them represent a considerable hazard to living organisms (Li et al., 2014). One of the major contributors to the airborne aromatic compounds, including their gas-phase and particlebound fractions, is wood burning. Besides the most abundant natural polymer, cellulose-hemicellulose, wood comprises 20-35% of aromatic polymer lignin, which represents a unique source of atmospheric methoxyphenols with emission rates in the range 900-4200 mg/kg fuel (Simpson et al., 2005). In Dettenhausen, a German residential village, wood smoke was estimated to contribute 49% to the total PM<sub>10</sub> organic mass in winter (Bari et al., 2009).

After being emitted, aromatic pollutants undergo chemical processing in the troposphere; besides aging of organic compounds in the atmospheric gaseous phase and on the particle surface, tropospheric aqueous-phase transformations affect their lifetimes considerably in conditions of cloud droplets, fog, and wet aerosols (Harrison et al., 2005; Lim et al., 2010). However, aromatic aqueous-phase aging is only rarely included into atmospheric models, which deviate substantially from field measurements. Therefore, there is a huge need for kinetic parametrization of processing of aromatic compounds which can be used in global atmospheric models.

Very recently, a powerful experimental-simulation tool for the determination of kinetic rate constants of semi-volatile lowand aromatic pollutant transformations in the tropospheric waters was introduced (Kroflič et al., 2015a). Long-term reaction profiles nicely showed that, in a frame of nitration of aromatic compounds in the presence of nitrite under acidic aqueous conditions, it is very important to account also for the electrophilic aromatic substitution by nitronium ion (NO2<sup>+</sup>). The applied novel approach to study the kinetics of aqueous-phase aging of tropospheric pollutants allows the determination of relevant kinetic rate constants of reactions between organic compounds and distinct reactive species with a great deal of confidence.

#### State of the Art

Wood lignin mainly consists of coniferyl and sinapyl alcohol units, the latter being present only in hardwoods. During the incomplete wood combustion, softwood and hardwood burning, guaiacol (GUA) and its derivatives are emitted into the troposphere. GUA analogues are thus ubiquitous in wood smoke coming not only from forest fires but also from domestic stoves and fireplaces. Especially in residential areas, wood combustion can account for over 90% of the wintertime ambient PM with large amounts of biomass burning pollutants, many of which are known carcinogens (Bari et al., 2009). In the presence of atmospheric reactive nitrogen, nitro-aromatic compounds can form, which are often coloured – thus contributing to the atmospheric brown carbon budget – and hazardous for human health and other living organisms (Kovacic and Somanathan, 2014).

Nitration of GUA (0.1 mM) was studied in acidic H<sub>2</sub>SO<sub>4</sub> solution, typical for the atmospheric waters (pH 4.5), upon addition of  $NaNO_2$  and  $H_2O_2$  in the dark and under simulated sunlight conditions (solar simulator LOT-QuantumDesign Europe, Darmstadt, Germany, equipped with a 300 W ozone free xenon short arc lamp). The investigation revealed that 4- and 6nitroguaiacol (4NG and 6NG, respectively) are preferentially formed. After a short lag time, 4,6-dinitroguaiacol (DNG) also starts to form and its production substantially accelerates after GUA is completely consumed. A complex reaction scheme was needed to be proposed for aqueous-phase nitration of GUA under mild acidic conditions and is represented in Figure 1. The therefrom derived model function described well experimental data obtained under different experimental conditions.





Fitting of the model function was performed simultaneously to a series of independent experimental data; global kinetic parameters of the proposed reaction pathways were determined with a fair amount of confidence ( $R^2 = 0.9958$ ). The set of differential molar balances, derived according to the proposed reaction scheme, was numerically solved in Matlab 7.12.0 (MathWorks, Natick, MA, USA). Rosenbrock algorithm (orders 2 and 3) with adaptive step size control (step as low as 10-7 h was initially required) had to be used to overcome the problem of simultaneous numerical solving of differential molar balances of nitrogen-containing reactive species (NRS) and methoxyphenols. Kinetic rates of methoxyphenol nitration/nitrosation and NRS formation/termination may differ by several orders of magnitude; serious problems in numerical stability of the system were caused in particular by fast reactions.

#### **Reaction Model**

In the dark,  $HNO_2/NO_2^-$  and  $NO_2^+$  are known nitrating agents of aromatic compounds in acidic NaNO<sub>2</sub> solution (Park and Lee, 1988), but our modelling study ruled out the HNO<sub>2</sub>-driven mechanism in the case of GUA. Notwithstanding, experiments of individual nitration of 4NG and 6NG revealed that there must be another nitrating agent beside  $NO_2^+$  in the reaction mixture even in the absence of hydrogen peroxide in the dark.  $NO_2^+$  was proposed and its formation explained with the existence of a redox system in the presence of dissolved oxygen from air.

In the presence of  $H_2O_2$ , aqueous-phase nitration of aromatic compounds is largely affected by formation of peroxynitrous acid (HOONO) at low pH, which can yield OH<sup>•</sup> and NO<sub>2</sub><sup>•</sup> radicals and other nitrating agents such as NO<sup>+</sup> and NO<sub>2</sub><sup>+</sup> (Vione et al., 2003). Our study showed that formation of NO<sub>2</sub><sup>•</sup> is not crucial for matching of the model with experimental data, whereas NO<sub>2</sub><sup>+</sup> is essential to properly describe obtained concentration profiles.

Upon illumination, nitrite and in particular nitrous acid decompose into OH<sup>•</sup> and NO<sup>•</sup> and also yield NO<sub>2</sub><sup>•</sup> in the reaction with hydroxyl radicals (Vione et al., 2003). In order to avoid unnecessary fitting parameters, which we believe would not substantially improve the represented study, mass balance of OH<sup>•</sup> radicals, nitrate/nitric acid (NO<sub>3</sub><sup>-</sup>/HNO<sub>3</sub>) photolysis, and formation of radiation-excited nitrite (NO<sub>2</sub><sup>-\*</sup>) are not accounted for in the model.

In the proposed reaction scheme, nitrosation (with both NO<sup>•</sup> and NO<sup>+</sup>) is regarded as the only sidereaction pathway, although there is an evidence for hydroxylation especially at 4NG nitration upon illumination. Apparent kinetic rate constants for reverse reactions, converting NRS into either HNO<sub>2</sub> or HNO<sub>3</sub>, were considered in the reaction model to control low concentrations of NRS during the fitting procedure.

#### **Experimental Results and Discussion**

Modeled concentration time profiles of GUA and its nitration products, as well as NRS, are shown next to the experimental data points of 0.1 mM GUA nitration under simulated sunlight conditions upon addition of 1 mM NaNO<sub>2</sub> and  $H_2O_2$  (Figure 2). Focusing on the experimental results, which are represented by symbols, a special attention should be paid to the sigmoidal behavior of DNG. A prominent inflection cannot be described by the radical reaction mechanism actually, because free radicals typically react with high absolute rate constants that do not deviate for more than one order of magnitude (Herrmann et al., 2010). In contrast, electrophilic reactive species exhibit substantial differences in their affinity towards distinct aromatic compounds (Carey and Sundberg, 2007) and were thus considered promising candidates for targeting the drastic change observed in DNG concentration profile.



Figure 2. Experimental data (symbols) and modelled concentration profiles (lines) of guaiacol (GUA) nitration in acidic H<sub>2</sub>SO<sub>4</sub> solution (pH 4.5) upon addition of NaNO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> under simulated sunlight conditions. Ar conc stands for concentrations of GUA, 4- and 6-nitroguaiacol (4NG and 6NG, respectively), and 4,6-dinitroguaiacol (DNG). (Adapted from Kroflič et al., 2015a)

It can be concluded from our modelling study and the literature data survey, that electron-withdrawing nitro substituent deactivates the aromatic ring and substantially supresses its susceptibility for electrophilic attack. Second-order kinetic rate constants of electrophilic nitration of GUA were found up to four orders of magnitude higher than electrophilic nitration rate constants of nitroguaiacols. In the beginning of the experiment, major portion of NO2<sup>+</sup> is therefore scavenged by GUA, whereas DNG formation pathway is a minor consumer of nitronium ion. After GUA is completely consumed, only mono-nitro and other less activated derivatives of GUA compete for NO<sub>2</sub><sup>+</sup>, which considerably increases its steady-state concentration in aqueous solution and accelerates formation of secondgeneration nitration products. The resulting NO2<sup>+</sup> concentration profile is shown in Figure 2 and should be compared with much less prominent concentration dependence of NO2<sup>•</sup>. As a consequence of electrophilic aromatic substitution, accumulation of the highergeneration nitration products of the primary aromatic pollutant can be assumed in the regions downwind of the BB source. Moreover, in the analogy to other nitroaromatics, multi-nitro derivatives can be considered the most toxic (Artemenko et al., 2011), which even strengthens the importance of electrophilic nitration in the environment.

Although the second-order kinetic rate constants of electrophilic nitration of GUA are much lower than the

corresponding rate constants of GUA radical nitration, both mechanisms were found competitive under investigated conditions because of substantially higher concentrations of electrophilic nitrogen-containing reactive species estimated in aqueous solution. Furthermore, environmental importance of the observed sigmoidal behavior of DNG formation was also studied by simulating bulk concentration of NO<sub>2</sub><sup>+</sup> vs. nitrite concentration at different nitrite-to-GUA ratios. The investigation revealed that the concentration window, where aromatic compounds compete for NO2<sup>+</sup> in tropospheric waters, is relatively broad, which is not the case with  $NO_2$  (Figure 3). Electrophilic nitration should be therefore kept in mind when considering transformations of low- and semi-volatile aromatic pollutants in the atmospheric aqueous phase.



Figure 3. Bulk concentration of  $NO_2^+$  and  $NO_2^-$  vs. nitrite concentration in the dark at different nitrite-to-GUA ratios (Re = 1–1.000.000). Grey lines represent experimental Re of 10. (Adapted from Kroflič et al., 2015b)

#### Conclusions

The represented study emphasizes the important role of electrophilic species for transformations of aromatic compounds in the atmospheric waters and underlines the consequential threat for remote biotopes, i.e. rain forests and oceans. It discusses the competitiveness between aromatic pollutants for distinct reactive species in the tropospheric aqueous phase and explains the conceptual differences between them from the kinetic perspective.

#### Acknowledgments

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# KINETIC STUDIES OF THE ATMOSPHERICALLY IMPLICATED HALOGEN OXIDE RADICAL AND PEROXY RADICAL CROSS-REACTIONS

Michael K. M. Ward<sup>\*</sup>and David M. Rowley CNRS/ Université Lille 1 – Labo PC2A Villeneuve d'Ascq, F-59655

Keywords

Halogen oxide, Peroxy radical, Laser flash photolysis, CCD detection.

The occurrence of halogen oxide radicals, XO (X = Cl, Br, I), has a profound impact on atmospheric chemistry [1]. XO, formed from the reaction of X + O<sub>3</sub>, can react with peroxy radicals, RO<sub>2</sub>, which are key members of the so called "odd hydrogen" radical family, HO<sub>x</sub>. These reactions may enhance O<sub>3</sub> loss or affect the oxidising capacity of the atmosphere. Detailed laboratory studies of the kinetics of reactions of the type XO + RO<sub>2</sub>  $\rightarrow$  Products, for inclusion in models, are therefore important in understanding the atmospheric implications of such chemistry.

The kinetics of several XO + RO<sub>2</sub> (X = Cl or Br and R = H or CH<sub>3</sub>) reactions have been studied as a function of temperature (T = 210 - 314 K) at  $p = 760 \pm 20$  Torr, using the laser flash photolysis technique coupled with UV absorption spectroscopy, employing a charge coupled device (CCD) detection system for broadband, time resolved monitoring of radicals. Exploiting the vibronic structure characteristic to XO radicals *via* 'differential' spectroscopy afforded unequivocal monitoring of [XO] [2]. [XO] profiles were then analysed using detailed numerical models. Strict control of successive experimental conditions and constraints in each fitting model used allowed the initial [RO<sub>2</sub>] to be inferred and their temporal behaviour were simulated alongside the measured temporal [XO] profiles to obtain kinetic information on each reaction investigated.

The determined  $ClO + HO_2$ ,  $ClO + CH_3O_2$  and  $BrO + HO_2$  reaction rate constants will be presented and their temperature dependences discussed and compared with previous work and the current JPL NASA recommendations [3]. The sensitivity of each kinetic model applied in determining the kinetic parameters for each reaction studied has also been investigated.

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# Revisiting the Kinetics of Selective Hydrogenation of Phenylacetylene over an Egg-Shell Catalyst

Zhiming Zhou<sup>\*</sup>, Jiawei Hu

State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

Keywords

Selective hydrogenation, Kinetics, Diffusion, Catalyst, Model.

Liquid-phase selective hydrogenation of phenylacetylene plays an important role in the posttreatment of pyrolysis gasoline (pygas), a byproduct of naphtha pyrolysis. Considering the relatively high reaction rates and the strong effect of mass transfer on the selectivity, egg-shell catalysts with a very thin Pd layer on Al<sub>2</sub>O<sub>3</sub> are generally used.<sup>[1]</sup> To date, most investigations on reaction kinetics over egg-shell catalysts can be classified into two main categories: (1) the catalyst is simplified as a particle with uniform activity, in spite of the fact that the active Pd layer is only several tenths micrometer; and (2) a rate constant density function or so-called activity distribution factor (defined as the ratio between the local rate constant and its volume averaged value) is introduced to describe the non-uniform activity distribution of the egg-shell catalyst. Although many studies in literature seem to show that the above methods can phenomenologically describe the kinetic behaviors over egg-shell catalysts, there are still questions to be answered, e.g., whether the influence of mass transfer processes is really negligible? Whether the concentration profiles in the active layer of the catalyst is accurately described? In fact, our recent work<sup>[2]</sup> has demonstrated that for the selective hydrogenation of cyclopentadiene, the influence of internal diffusion limitations is noticeable despite the use of an egg-shell catalyst.

Here, the reaction kinetics of phenylacetylene hydrogenation is studied in a trickle-bed reactor using a home-made egg-shell Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. Experimental results clearly show that the effect of mass transfer on the activity and selectivity is evident and therefore, a rigorous model is developed. At the catalyst scale, the diffusion and reaction of different species in the thin active layer is depicted. The diffusion flux is expressed by the Fick's law and the kinetic model is derived by assuming a two-step adsorption for organic species. At the reactor scale, an axial dispersion model including the liquid-solid mass transfer is considered. The kinetic and adsorption parameters involved in the kinetic model are finally estimated with the experimental data by using the Levenberg-Marquardt method, which minimizes the sum of squares of relative residuals between the measured species concentrations and the model-calculated values.

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# Experiments and modeling of after-treatment options for alternative fuel based engines

Snigdha sree R.\*, Preeti Aghalayam Indian Institute of Technology Madras Chennai, India-600036

## Abstract

Different reaction mechanisms have been proposed for NO reduction by PGM under automotive exhaust conditions. Although several researchers have discussed them, several uncertainties remain still. The scope of this work involves development and validation of quantitative reaction mechanisms. A lab-scale experimental facility has been set up with a packed bed reactor of pellets of platinum on alumina. NO, with different reductants such as CO and propene, is passed into the reactor over the platinum catalyst. The extent of NO reduction is studied for different reactor temperatures and different inlet feed compositions, using a chemiluminescent analyzer. The experimental data is used to validate a global rate expression derived from a micro-kinetic model developed in the group. The model is observed to agree well with the experimental data. Similarly, NO is reduced in the presence of propene, NO reduction is calculated for different temperatures and feed compositions and the data obtained is used to validate a global reaction rate model.

#### Keywords

NO reduction, Selective catalytic reduction (SCR), Platinum group catalysts

#### Introduction

Nitrogen oxides are air pollutants that cause acid rain and photochemical smog. As carcinogens, they are also harmful to human health. As a result, stringent regulations have been imposed on their emissions. To meet these stringent emission standards, several in-cylinder and after-treatment techniques are being used but each of these technologies has their own limitations. Among all the techniques available for  $NO_x$ abatement, selective catalytic reduction (SCR), an after treatment technique, in which  $NO_x$  is reduced to diatomic nitrogen using a reductant over a suitable catalyst, is promising for automotive applications as  $NO_x$  can be reduced up to 70 to 90% depending on the catalyst design, application and injection strategy.

SCR is the process of reducing  $NO_x$  to diatomic nitrogen using a reductant usually termed as "Diesel exhaustive fluid" and a catalyst. The exhaust is first mixed with the reductant and the mixture is then passed over a catalyst where the reaction between the  $NO_x$  and reductant is promoted and  $NO_x$  is reduced to Nitrogen and water vapor. Many reducing agents such as soot, ammonia, urea and hydrocarbons have been used in SCR. Out of these, hydrocarbons are a good choice as unburnt hydrocarbons are readily available in engine exhaust unlike the other reductants for which a special chamber has to be provided in the system. Furthermore, in the case of urea and ammonia, stoichiometric control of  $NH_3$  to avoid ammonia slip is a matter of concern [Lanza et al., 2009].

Cu-ZSM-5 was first reported as an effective catalyst for the SCR of NO by hydrocarbons in the presence of excess oxygen [Long and Yang, 1998]. Since then, the SCR of NO has received much attention as a potential technology for cleaning NO in various oxygen-rich exhausts of diesel engines. Alumina supported silver catalysts (Ag/Al<sub>2</sub>O<sub>3</sub>) which are durable and inexpensive are also considered to be a candidate for practical use. However, NOx conversion over Ag/Al<sub>2</sub>O<sub>3</sub> is quite low at a temperature range of 300-400 °C, which is a major disadvantage considering that the temperature range is especially important for diesel engines exhaust. Zeolite-based catalysts can be particularly effective for the selective catalytic reduction (SCR) of NO with methane (e.g. Co or Ga/ZSM-5) or propene (e.g. Cu/ZSM-5). However, the hydrothermal resistance of these materials is usually unsatisfactory [Burch et al., 2002].PGM catalysts especially Platinum have been reported to be efficient for HC-SCR due to low temperature activity, and water tolerance, as compared to the other zeolite based catalysts [Lee and Kung, 1998].

#### **PGM catalysts**

The extent of NO*x* reduction by hydrocarbons that can be achieved using PGMs is very dependent on the choice of PGM and on the chemical nature of the hydrocarbon reductant [Engler et al., 1995]. The following figure shows typical results for the various PGMs for NO*x* reduction by propene which shows that in this case Pt is the most active and selective metal at lower temperatures.



<sup>•</sup> Preeti Aghalayam, preeti@iitm.ac.in

# **Fig 1:** Activity of 1% Rh, Pd and Pt supported on SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> in the reduction of No by C<sub>3</sub>H<sub>6</sub> [Burch et al., 2002]

Under lean-burn conditions, the reduction of NO on Pt by strongly adsorbing hydrocarbons produces typical volcano-type profiles as a result of the competition of two oxidation reactions in which either molecular oxygen or nitrogen oxides can be the source of oxygen. Molecular oxygen is the main source above the peak in NOx conversion and the hydrocarbon reductant is eventually completely consumed unproductively (i.e. NOx reduction diminishes to zero as the temperature is raised further). Below the peak temperature, NOx reduction occurs on a reduced Pt surface containing hydrocarbonaceous residues [Burch et al., 2002].

# Proposed mechanisms for reduction of NO on pt by propene type hydrocarbons:

Three distinct mechanisms have been proposed for lean deNOx on Pt. These are:

- i. The intermediacy of cyanide or isocyanate (-CN or -NCO) surface species
- ii. The intermediacy of organo-nitro and related species (e.g. R-NO<sub>2</sub>, R-ONO)
- iii. NO decomposition and subsequent oxygen removal by the hydrocarbon reductant.

In some circumstances more than one of these mechanisms could act simultaneously [Burch et al., 2002].

Thus there are different proposed mechanisms, attempting to explain the same process. Thus, the exact reaction mechanism and kinetics for  $NO_x$  reduction is not yet well established. This work focuses on developing kinetic models for after-treatment devices especially HC-SCR by

- developing a reactor-scale experimental set up
- conducting experiments with diesel engine exhausts
- predicting the engine out NO<sub>x</sub> and calculating NO<sub>x</sub> reduction
- Validating the reaction-models with the data thus obtained from the experiments.

## Experimental set-up:

The experimental set-up consists of gas cylinders of the reactant gases (NO, HC and  $O_2$ ) the flow of which is controlled by mass flow meters .These gases are allowed into a fixed bed reactor with platinum catalyst pellets which were packed in a catalyst holder. This reactor is placed inside a furnace in which the reaction takes place. The furnace has the provision to measure the temperatures at different locations inside it. The outlet gases from the furnace are then sent through a chemiluminiscent analyzer which measures the concentration of NO. The conversion of NO can be calculated from the inlet and

outlet concentrations and at different temperatures and feed compositions.



Fig 2: Schematic representation of experimental set-up

#### **Global rate expressions**

Global reactions when NO reacts with CO:

$$2NO + 2CO \le N_2 + 2CO_2$$
$$2NO + CO \le N_2O + CO_2$$

Mantri &Aghalayam proposed the micro-kinetic model for the above system and validated it against suitable experimental results. This micro-kinetic model consists of 8 reversible reactions. Activation energies are calculated using UBIQEP method and pre-exponential factors and sticking coefficients are taken from literature for these elementary reactions. Solution to the micro-kinetic model is obtained for the plug flow reactor geometry, using the ChemKin library routine. The model is validated by comparing the obtained results with experimental results from the literature. The micro-kinetic simulations require solving for simultaneous differential equations arising from gas phase mass balance such as

$$(\rho u)\frac{dy_i}{dz} = \left(\frac{a}{V}\right) M_t \sum_j \vartheta_{t,j} r_j \qquad for \ i = 1, \dots, N_g$$
(1)

and algebraic equations arising from quasi steady state conditions of surface species

$$\sum_{j} \vartheta_{i,j} r_{j} = 0 \qquad for \ i = 1, \dots, N_{s} - 1$$
(2)
and
$$\sum_{i=1}^{N_{s}} \theta_{i} = 1 \qquad (3)$$

where



Solving the above equations is the most suitable approach for small to moderate size mechanisms but becomes computationally expensive and tedious in case of larger mechanisms, which is the usual case with PGM catalysts. Solving explicit global rate expressions minimize the computational time and cost. Hence, taking the above micro-kinetic model as the basis, global rate expressions for the NO-CO system on platinum has been developed in the group using sensitivity analysis method. The rate expressions are as follows:

$$r_{N_2} - r_5 - r_6 - k_5 \theta_N^2 - k_6 p_{N_2} \theta_{p_1}^2 - (k_5 w^2 - k_6 p_{N_2}) \theta_{p_1}^2$$
(4)

$$r_{N_20} = r_9 - r_{10} = r_7 - r_8 = \kappa_7 \sigma_{N0} \sigma_N - \kappa_8 \sigma_{N_20} \sigma_{Pt}$$
(5)

Where

$$w = \frac{-k_7 K_{N0} p_{N0} + \sqrt{(k_7 K_{N0} p_{N0})^2 + 8k_5 k_8 K_{N0} p_{N0} + 16k_5 k_6 p_{N_2} + 8k_5 k_8 K_{N_0} p_{N_0} 0}{4k_5}}{4k_5}$$
(6)

The above rate expressions could simulate the microkinetic results well.

### **NO-CO** experiments

The first set of experiments is carried out with NO and CO so as to validate the data obtained from these experiments with the model already developed in the group for NO-CO system.

The outlet concentration of NO is measured for temperatures from 50-700 °C at 50 °C intervals. NO conversion is calculated from the inlet and outlet concentrations at different temperatures and for different feed compositions.

There is very little emphasis on the effect of feed composition (i.e., the ratio of reductant to NO) on the extent of NO conversion in the literature. Even though a little information is available, most of the results are based on simulations. Hence, we expect that the results from our experiment provide us with some insights on the effect of feed compositions, once these results are validated with the model. Experiments were conducted with 1:1 NO and CO (i.e., 1 liter per minute of 1000 PPM NO and 1 liter per minute of 1000 PPM CO) and 1:2 NO and CO and the results are compared.

The %conversion of NO at different reaction temperatures is plotted for both 1:1 NO-CO and 1:2 NO-CO as shown in the figure below.



Fig 3: Comparision of % NO conversion at 1:1 and 1:2 NO-CO

From the above results, it is evident that as the amount of CO in the feed is doubled, the conversion is increased by nearly 10%. Nevertheless, there is a qualitative difference between the results reported both from the literature as well as from previous experiments in the group. In the absence of oxygen in the system, the conversion of NO is supposed to increase to a certain temperature and then remain constant thereafter, whereas the conversion decreases after reaching a maximum if oxygen is present in the system. This is the result of the competition of two oxidation reactions in which either molecular oxygen or nitrogen oxides can be the source of oxygen. Molecular oxygen is the main source above the peak in NO<sub>x</sub> conversion.

But, here in our experiments, we could see a drop in the NO conversion even though oxygen is not present in the system. This is a result of decrease in the surface area of the catalyst after the reaction. The surface area of the catalyst is determined before and after the reaction using the BET surface area analysis. The surface area of the catalysts which is  $90m^2/g$  before the reaction, decreased to  $68m^2/g$  after the reaction. The peak temperature can be attributed to this change in the surface area of the catalyst.

# Validating the model

NO outlet concentrations from the experiments and those from the model are compared as shown below.



Fig 4: comparison of experimental and simulation outlet NO concentration for 1:1 NO-CO



Fig 5: comparison of experimental and simulation outlet NO concentration for 1:2 NO-CO

Most of the literature reports that, on platinm catalyst, NO conversion reaches 100% between 250 and 300 °C and then remains constant even at higher temperatures in the absence of oxygen. The lower NO reduction in our experiments can be a result of the catalyst structure, which is pellets in our case, and a higher Gas Hour Space Velocity (GHSV) of the reaction. When equation (1) is used in the simulations, the model gives 100% NO conversion at 250°C. But, the equation is valid for a PFR where the total volume of the reactor is available for the reaction. But, the reactor in our case is a Packed Bed Reactor (PBR)

where the reaction takes place only on the surface of the catalyst and hence the porosity or the void fraction in the reactor has to be considered. Thus, When the PFR equation is changed accordingly to define the rate based on the weight of the catalyst and when the porosity of the reacor is included, (1) becomes

$$V(1-\Phi) \rho u \frac{dy_i}{dz} = WM_i \sum_j \vartheta_{ij} r'_j \quad for \ i = 1, ..., N_g \quad (7)$$

When the above equation is used, the model also predicts the maximum conversion of NO at 450-500 <sup>o</sup>C matching better with the experimental results as shown in the figures 4 and 5. The pellet structure of the catalyst, the effect of pressure drop due to the pellets and the high GHSV in our experiments can be posible reasons for the differences between the experimental and modeling results. The following figure shows the effect of GHSV on the outlet NO concentration. It can be seen that as GHSV increases, the temperature at which outlet NO concentration becomes zero, increases, which is in line with our results.



Fig 6: Effect of GHSV on outlet NO concentration

#### **NO-HC Experiments**

The choice of hydrocarbon has a lot of effect on the performance of the platinum catalyst in reducing NO. Alkenes are reported to be better reductants than alkanes. For example, propene is reported to be a better reductant than propane. This is due to the tendency of propene to adsorb on to the surface of the catalyst better than propane [Burch et al., 2002].

In the present study, propene is used to reduce NO. Most of the literature reports NO reduction with propene in presence of oxygen. In the presence of oxygen, 100% of NO conversion is achieved at around 300 °C on Pt/Al<sub>2</sub>O<sub>3</sub>. But, when the experiments are carried out in the absence of oxygen, maximum NO reduction is observed to be only around 15-20%, at 300 °C itself when the amount of propene is twice that of NO in the feed. When both are in equal amounts, the NO reduction is much lesser that this 20% which is of no interest to us. NO conversion at different reaction temperatures is shown in the figure 7 for 1:2 NO-Propene.

A global rate expression for the reduction of NO with propene on platinum catalyst is not readily available in literature. Hence, we are trying to derive a global rate expression from the micro-kinetic model available in



Fig 7: % NO conversion at 1:2 NO-Propene

the literature that is most suitable to our experimental conditions. Once the expression is derived, it would be validated with the experimental data. **Conclusion** 

An experimental facility to carry out the Selective Catalytic reduction of NO has been set up and experiments are carried out with different reducing agents such as Propene and CO. NO conversion is calculated at different reaction temperatures and various feed compositions. The results show that for 1:1 NO-CO the conversion is around 70% and for 1:2 NO-CO it is 80% resulting in 10% rise in the conversion when the amount of CO is twice that of NO in the feed. There is a drop in the conversion of NO after the peak temperature because of loss in the surface area of the catalyst after the reaction.Experimental data obtained is used to validate a global reaction model, for NO-CO system, already developed in the group. Similarly NO is reduced with Propene in the absence of oxygen and the conversion is found to be very less around 15-20%. The experimental data will be used to validate the global rate expression which is yet to be developed.

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# KINETICS OF CATALYTIC CARBON GASIFICATION: GEOMETRY, LINEARITY, "CARBONWORMS", "CASA" FRONT

L Sousa Lobo<sup>1,\*</sup>, SAC Carabineiro<sup>2</sup>; MANDA Lemos<sup>3</sup>, F Lemos<sup>3</sup> (1) Requimte Research Center, U. Nova de Lisboa, Portugal; (2) LCM, Laboratório Associado LSRE/LCM, FEUP, U. Porto, 4200-465 Porto, Portugal; (3) CERENA, IST, U. Lisboa; <u>\*sousalobo266@gmail.com</u>



Introduction. Carbon gasification is an important topic nowadays in view of the energy market. bioenergy trends and biorefinery concept, which are expanding due to the recent political and economic developments. The mechanism of catalytic carbon gasification has been recently reviewed (Lobo, 2013). Evidence that the prevailing mechanism involves carbon bulk diffusion has been also emphasized (Lobo, 2014). The mechanism has been originally proposed 30 years ago to explain the catalytic effect of K<sub>2</sub>CO<sub>3</sub> and MoO<sub>3</sub> in the following terms: "The linearity of the loss of weight versus time curves observed with MoO<sub>3</sub> and with  $K_2CO_3$  at low temperatures suggests that a constant reaction front is operating throughout the reaction process. That reaction front should be the sum of the contact areas of all particles or droplets acting as catalyst. It is pertinent to pose the question of where the oxidizing gas meets the carbon surface" "Three phases would take part in the reaction. A gas phase; a solid phase, which is the second reactant, carbon; a third phase (liquid or solid) is operating in between as a catalyst. If carbon atoms are even slightly soluble in the catalyst and diffuse through it easily, this mechanism explains the kinetics and behaviour There is good evidence that understanding the kinetics of catalytic carbon gasification involves the use of Fick's Law at nanolevel, evaluating the relative rates of carbon dissolution, carbon bulk diffusion through the catalyst and surface gas/ catalysis. Linearity of the weight versus time dependence up to more than 50% conversion indicates that a stable carbon bulk diffusion mechanism is taking place. dependent moving catalyst The size nanoparticles observed under in-situ microscopy and the reaction orders are both well explained by this mechanism.

observed" (Silva and Lobo, 1986).

The CASA front. The intrinsic kinetics in the case of catalytic carbon gasification is assumed to be based in the "contact active surface area" (CASA). This explains linearity in the w (weigth) vs. t (time) plot (Fig. 1) and the observation of the fast and slow moving particles under *in-situ* electron microscopy. In this case the carbon mass transfer takes place at the nano level. The kinetic model requires coupling surface catalysis with



Figure 1. Catalyst nanoparticles move under reaction conditions like carbon worms ("eating" carbon), forming an overall reaction front: CASA. This predicts perfect kinetic linearity when the reaction front is stable (channelling) or somewhat curved when changes in the reaction front take place progressively (edge recession or channelling with lateral recession).

Fick's laws (which postulate that the flux goes from regions of high concentration to

low concentration, with a magnitude that is proportional to the concentration gradient (Fick's 1st law):

$$\mathbf{J} = -\mathbf{D}\frac{dC}{dx}$$

where J is is the diffusion flux (or the amount of substance per unit area per unit time), D is the diffusion coefficient or diffusivity, C is the concentration assuming steady state conditions (amount per volume), and x is the position (or lenght). During the initial induction period solid-state changes may occur, as the temperature and the contact with reactant gas may alter the solid phase(s) present. Those initial changes can be modelled using Fick's second law (t is the time):

$$\frac{\partial C}{\partial t} = D \, \frac{\partial^2 C}{\partial x^2}$$

Once those reactions are complete, a carbon steady-state bulk diffusion process will be operating, governed by Fick's 1st law. In short, we may summarize the approach to model the nano mass transfer processes taking place: Use Fick's laws: first the 2nd, then the 1st.

When the geometry of the CASA front is stable linearity will be observed (Fig. 2), but with a liquid and expanding CASA front (check Fig. 1B) an acceleration of the rate will be observed and strict linearity is not observed. This is the case with alkali metal catalysts at high temperatures (Fig. 3).



Fig. 2. Catalytic carbon gasification by Mo, by K and by the two metals combined. The observed reaction orders evidence the nature of the slow and rate-controlling step.

**Observed kinetics, reaction orders, particle size effect.** The study of carbon gasification using different gases, various catalysts - excluding alkaline ones - showed an overall prevalence of a linear behaviour in observed kinetics of Fig. 4 (Carabineiro, 2000: Carabineiro et al., 2001). We find that when the incipient wetness method is used to impregnate the catalyst, the initial transition period (2nd Fick's law) is so short that kinetics of those fast changes are not easily followed. An important factor in kinetics is reaction orders. When the carbon bulk diffusion step is rate controlling the observed order to the reactant gas pressure is zero. On the other hand, when the surface reaction is slow it will be rate controlling and the order may be one or close to it. This is shown in Fig. 2 in connection with the separate and combined effects of potassium and molybdenum (impregnation with K<sub>2</sub>CO<sub>3</sub> and MoO<sub>3</sub>) (Silva and Lobo, 1986). With Mo catalyst the reaction order is 1 because the carbon bulk diffusion is fast as compared with the surface reaction rate  $(CO_2 + C = 2)$ CO). On the other hand, with K the reaction order is zero: carbon bulk diffusion is the slow step. The combined effect of the two catalysts shows some synergetic effect and the reaction order evidences the easy carbon bulk diffusion.

When observed under in-situ transmission electron microscopy the rate of movement of the catalyst particles changes with size, but in certain systems the small particles move faster and in other systems the big particles move faster. This depends in fact of the controlling step and so of the reaction order, as explained in Fig. 5 (Lobo, 2013).

**Synergetic effects.** When two metals are mixed, a synergetic effect is sometimes observed, which means that the effect is superior to the sum of the effects observed by each of them (Figs. 2 and 5). How should one interpret this effect? How can we plan experiments to better understand it? There are good chances to find less expensive and more efficient catalysts operating at lower temperatures.

The synergetic effect may be due to geometry (smaller and more numerous catalyst nanoparticles), more active surface catalysis or higher carbon bulk diffusivity. The driving force for diffusion must be seen as a dynamic equilibrium (Lobo, 2013). Grabke discussed solid-state equilibria in Fe doped Boudouard



Fig. 3. Carbon gasification by K and Mo combined show a change from linearity to an expanding CASA front above 770°C (acceleration of the rate), probably due to the liquid nature of the catalyst above that temperature.



Fig. 4. Expected dependence of the rate of carbon gasification with size and with prevailing kinetics: nature of the rate-determining step (Lobo, 2013).

reaction (Grabke, 1972). This was further discussed by us recently (Lobo, 2013). The size of the particles may change with the preparation method (annealing, fast or slow cooling, etc.). The effect of V in reducing grain size in alloys was observed 30 years ago (Enami *et al.*, 1982). A comprehensive review on alloy catalysts was published, but it just covers surface catalysis, not catalysis with bulk diffusion (Ponec, 2001). The role of nanoparticles in catalysis is recognized (Toshiba, 2011).



Fig. 5. Normalised weight loss curves ( $W/W_0$ ) of the carbon impregnated with Fe, Cu, Mg, V and their V alloys in CO<sub>2</sub> at 600°C (adapted from Carabineiro, 2000).



Fig. 6. TGA/DSC analysis of carbon gasification by  $O_2$  catalyzed by 1% vanadium. The initial solid-state changes are complete 6 mins after the system reaches the reaction temperature. No further changes seem to operate during the following kinetically linear steady-state gasification.

In recent TGA/DSC studies of gasification by  $O_2$  using V, after the initial solid-state reactions occurring after the fast temperature rise for a few minutes, a linear steady-state weight loss is established. A flat profile of the DSC register is observed: evidence that the initial solid-state changes stopped (Fig. 6).

Active solid-state phases. The effective catalysts in carbon gasification must have the following properties: 1) Active contact with carbon; 2) Easy carbon dissolution; 3) Easy carbon diffusion: 4) Be active in surface catalysis between reactant gas and emerging carbon atoms. The active contact requires the catalyst to be at a temperature above the Tammann temperature, so that the active contact can be established (similar to the shape changes in sintering). This relationship has been found by Baker (see Figueiredo, 1986). The catalyst frequently changes phase when heated in the presence of the reactant gas. So, the phase present under reaction conditions may be a metal or an oxide, carbonate, hydride, or carbide. The melting points of the phases prevailing under given operating conditions is an important key to understand the catalvtic activity. The temperature of the particle under reaction may be higher (when the gasification is exothermic -v.g. using  $O_2$ ) or lower (when the gasification is endothermic- v.g. using H<sub>2</sub>O). Important clue: The solid phase operating in one side may be different from the solid phase operating on the other side when the bulk diffusion step is rate determining and a gradient of carbon concentration/ activity is established. The reaction order is an excellent key to know the nature of the rate determining step and the carbon concentration profile through the catalyst. However, the orders of reaction are usually not known when in-situ TEM is used.

**Conclusion:** kinetics is the key to understand the mechanism of catalytic carbon gasification and the operating conditions prevailing in a given gasification system. In the last 30 years, some 12 proposals for the mechanism have been advanced. Several reviews are available (McKee, 1981; Wood and Sancier, 1984; Figueiredo and Moulijn,1986; Moulijn and Kapteijn, 1995; Tomita, 2000; Toshiba, 2011), but the present mechanism is usually ignored.

When discussing mechanisms most authors take just a chemical approach, leaving aside carbon mass transfer, isothermal kinetic studies, dynamic solid steady-state equilibria and nano-geometry. Kinetics in fluids usually ignores geometry: the reactions are assumed to take place anywhere. Chemical equations are just listed. That is not the case with reactions involving the solid-state: geometry cannot be ignored. In addition, a solid-sate diffusion step shows an activation energy and a corresponding exponential temperature dependence. So, solid-state diffusion limited processes show a reaction type temperature dependence in Arrhenius plots.

Some studies based in solid-state *physics* use ab-initio approaches and undervalue kinetics. However, following Christiansen, *"Kinetics is more important than thermodynamics"* (Christiansen, 1964). Much progress can be achieved by joint work of kineticists with solid-state chemists.

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# HOW TO APPLY THE METHOD OF MOMENTS FOR POLYMERIZATION REACTIONS TO FISCHER TROPSCH SYNTHESIS (FTS)?

Luis A. Lozano G., Joris W. Thybaut\* and Guy B. Marin Ghent University, Laboratory for Chemical Technology – Ghent Technologiepark 914, Ghent, B-9052

# Abstract

A previously developed Single-Event MicroKinetic model for Fischer Tropsch Synthesis (FTS) on an Fe catalyst has been extended to a Co catalyst by accounting for CO insertion in addition to carbene insertion as the chain growth mechanism. The number of elementary steps that needs to be accounted for rapidly increases with the maximum carbon number that is considered in the network. The potential of the so-called 'method of moments', as applied in actual polymerization reactions, is explored for FTS which, indeed, is a polymerization-like reaction. A single moment has been defined for paraffins and 5 moments have been defined for the various types of surface species that need to be considered in the paraffins formation. Species with a carbon number below 5 are individually accounted for because they may exhibit deviations from the typical Anderson Schulz Flory behavior, while those with carbon number of 5 and higher are simulated by means of these moments. 0<sup>th</sup> order moments calculate global compositions by summations of species with an identical nature. This methodology has allowed restricting the size of the set of equations to only 37 regardless the extent of the reaction network with respect to carbon number. The gain in simulation time and effort is evident when realizing that a network limited to the formation of C<sub>10</sub> paraffins already relies on 72 elementary steps. Simulations based on the method of moments adequately reproduce the results obtained with the original model for C<sub>10</sub> paraffin products.

## Keywords

Fischer Tropsch Synthesis, Single-Event Microkinetics, method of moments, polymerization.

#### Introduction

The Fischer Tropsch Synthesis (FTS) is a catalytic reaction where syngas, a mixture comprising CO and  $H_2$ , is converted into long linear hydrocarbons and water, in the presence of a base-metal catalyst such as Fe or Co. The Fischer Tropsch products present a viable alternative to conventional crude oil because they consist of long hydrocarbons with minimal amounts of aromatics, sulfur, and heavy metals. More specifically, hydrocarbons with such characteristics constitute an ideal source for diesel fuels. The process has attracted particular interest in countries such as South Africa and Malaysia and Qatar where fully operational FTS reactors are operated (Dai et al., 2014).

The formation of these long hydrocarbons in FTS is believed to occur via a polymerization-like chain growth. In general terms, the product selectivity follows the so-called Anderson–Schulz–Flory (ASF) distribution. In a typical ASF distribution, the molar fraction of the products decreases at a constant slope with increasing carbon number. However, some peculiar deviations from this trend are encountered at lower carbon nunmbers. These deviations are often attributed to readsorption of low-carbon-number compounds on the catalyst surface or to symmetry effects. Also a changing dominant mechanism for chain growth may contribute to these discrepancies.

• Corresponding author: Joris Thybaut Joris.Thybaut@UGent.be

In this regard, different chain growth mechanisms have been extensively discussed in the literature. The different proposals are based on a specific type of monomer species which has not been properly identified, because it concerns a non-observable surface species. Basically, two possibilities are either the insertion of surface considered: methylene/carbene species (CH<sub>2</sub>) into the growing chain or the insertion of surface CO. Whilst many authors state that chain-growth happens due to the continuous addition of surface CH<sub>2</sub>, other researchers argue that the direct dissociation of CO and a subsequent hydrogenation to produce CH<sub>2</sub> is rather unlikely. However, the energy barrier to allow continuous additions of CO seems to be too high to enable the CO insertion. Finally, experimental evidence seems to validate the existence and the reactivity of the two monomers (van Santen et al., 2013). Figures 1 and 2 depict both mechanisms.

Apart from the debate on the actual chain growth mechanism, a second issue to be dealt with is the vast amount of surface reactions in FTS and the corresponding complexity of such reaction networks, which considerably increase the challenges for kinetic modeling (van Santen et al., 2013). Traditional approaches, such as power law equations, ignore the reaction mechanism complexity. Yet such models typically manage to reproduce the CO conversion but fail to adequately simulate product selectivities (Todic et al., 2013).

In order to properly describe the reactant conversion and product selectivity, it is necessary to

construct a kinetic model that manages to compile the underlying chemistry and, yet, relies on a reasonable number of rate equations. Furthermore, the goal of this work is to establish a compromise between the detail of the fundamental information and the extent of the reaction network, c.q., set of equations that needs to be solved, in order to facilitate kinetic analysis and to reduce the computational cost when performing simulations.



Figure 1. Schematic representation of the catalytic cycle for the carbene insertion according to Lozano (2008). \* indicates an active site.



Figure 2. Schematic representation of the catalytic cycle for the CO insertion according to Lozano (2008). \* indicates an active site.

MicroKinetic models aim at describing reaction networks in terms of all possible elementary steps (Dumesic and Rudd, 1993). A Single-Event model was previously MicroKinetic (SEMK) developed for an Fe catalyst (Lozano-Blanco et al., 2008) and it has been adapted as part of the present work, first by considering a Co catalyst and second by accounting simultaneously for CO as well as carbene insertion as the chain growth mechanism. The number of elementary steps in such a microkinetic model is so high that, when simulating hydrocarbon formation up to n-decane, already 72 elementary steps are required (Lozano-Blanco et al., 2008). The expansion of this network to simulate a realistic FTS product pool is expected to require more than 500 reactions.

It has previously been discussed that FTS exhibits similarities to polymerization reactions and,

hence, it is reasonable to explore typically used modeling strategies for polymerization reactions to reduce the number equations to be solved in FTS modeling. Among these approaches, the so-called 'Method of Moments' seems very attractive. It makes a summation of 'i' compounds of the same nature, where the categorization of the compounds into lumps is decided by the end-user.

In the present work, lumps have been defined for paraffins and surface species indicated in Figures 1 and 2 with carbon number 5 and higher. By doing so, the number of equations to be accounted for is reduced from several hundreds to merely 37 while retaining the fundamental chemical information and, therefore, satisfying the general goal of this work (Zabisky et al., 1992).

#### Procedures

In this work, the Method of Moments was implemented to describe the paraffins formation in FTS. The validation of the methodology was performed via comparison with the original model for the formation of hydrocarbons up to n-decane.

#### Kinetic Model

A SEMK model for Fe catalyzed FTS was developed by Lozano et al. (2008) and it was extended to a Co catalyst by eliminating the water gas shift reaction and incorporating the CO insertion mechanism next to the already included carbene insertion mechanism for chain growth.

In this model, H<sub>2</sub> and CO adsorption occur dissociatively and associatively, respectively. Once CO is adsorbed and subsequently dissociated on the catalyst surface, it undergoes step wise hydrogenations yielding surface CH<sub>2</sub> and CH<sub>3</sub> species. In 'polymerization terms' CH<sub>3</sub> is the initiator species from which a new chain can grow. Figure 1 depicts how chain growth occurs via the carbene insertion mechanism while Figure 2 shows the equivalent reactions according to the CO insertion mechanism. In both mechanisms, all surface R-CH<sub>2</sub> alkyl species are subject to the same 7 reaction types resulting in further chain growth or termination (reaction 7 in Figure 1-2). This potentially imposes important computational challenges for simulations since a realistic FTS pool of products that can easily contain up to  $C_{50}$ .

In the work performed by Lozano et al. (2008), kinetic parameters were estimated via SEMK model regression to experimental data. The number of adjustable parameters was reduced via an extension of the unity bond index-quadratic exponential potential (UBI-QEP) method to metallic surfaces.

#### Reactor Model

Simulations were performed in Athena Visual Studio (AVS) assuming an ideal plug flow reactor

(PFR). Operating conditions were set in the range of industrial low temperature FTS within a temperature range of 200 - 280 °C, pressure from 20 to 80 bar and varying molar ration  $H_2$ /CO ratio in the range of 1:1 - 2:1.

Due to the high stiffness of the set of equations describing the steady state operation of the reactor, a transient operation mode was considered to ensure a smooth convergence. The mass balance for the gas phase components in the PFR constitute a set of partial differential equations, Eq. (1), which were solved via discretization using the finite-difference method in the spatial dimension. For surface species the convective term is irrelevant and the mass balance is reduced to Eq. (2). Boundary conditions are described in Eq. (3).

$$\frac{\partial C_i^{g}}{\partial t} = -\frac{\partial F_i}{\partial V} + \rho_b \cdot R_i \tag{1}$$

$$\frac{\partial C_i}{\partial t} = R_i \tag{2}$$

$$V = \mathbf{0} \to C_i = C_i^{\mathbf{0}} \tag{3}$$

where:

$$\begin{split} \rho_{b} &: \text{bed density } (kg_{cat} \text{ } m^{-3}) \\ C_{i}{}^{g} &: \text{molar concentration in gas phase } (mol m^{-3}) \\ C_{i}{}^{s} &: \text{surface concentrations } (mol kg_{cat} - 1) \\ R_{i} &: \text{Net rate of formation } (mol kg_{cat}^{-1} \text{ } \text{s}^{-1}) \end{split}$$

The grid size effect on the numerical solution was assessed via the relative error in the n-decane molar flow rates as calculated according to Eq. (4), see Table 1. An acceptable grid size was achieved once the error lied within  $1.0 \times 10^{-3}$ .

$$Err = \frac{\begin{vmatrix} C_{C_{10}H_{22}}^{j} - C_{C_{10}H_{22}}^{j-5} \\ C_{C_{10}H_{22}}^{j-5} \end{vmatrix}$$
(4)

j: number of discretization points

Table 1. Influence of the number of discretization points on the relative error of n-decane.

points on the relative error of it declarer			
Number of discretization points 'j'	Error (-)		
10	0.0144		
15	0.0058		
25	0.0019		
35	0.0008		
40	0.0006		

Table 1 proves that this grid can be limited to 35 points.

#### **Method of Moments**

A moment ' $\lambda$ s' of a function 'Z(n)' is presented in Eq. (5).

$$\lambda_s = \int_{-\infty}^{\infty} n^s \cdot Z(n) dn \tag{5}$$

In this context, Z(n) may be either gas phase molar flow rates 'F<sub>i</sub>' or catalyst surface concentrations 'C<sub>i\*</sub>' of selected types of species with carbon number n for [n:  $n \ge 5$ ]. The 0<sup>th</sup> order moment then refers to the lump comprising all species of the same type. Five moment functions are defined for gas and surface species indicated in Figures 1 and 2. In Eq. (6-7) two examples can be found.

$$\lambda_0^{C_n H_{2n+2}} = \sum_{n=5}^{\infty} F_{C_n H_{2n+2}}$$
(6)  
$$\lambda_0^{C_n H_{2n+1}^*} = \sum_{n=5}^{\infty} C_{C_n H_{2n+1}^*}$$
(7)

These definitions simplify the calculation of the net rates of formation for the species in the reaction mechanism, e.g., let  $R_{CnH2n+2}$  be calculated according to Eq. (8). The terms  $r_{i,n}$  refers to reaction 'i' in Figures 1 and 2 for the compound of carbon number 'n'.

$$R_{C_n H_{2n+2}} = r_{7,n} \tag{8}$$

The summation from n=5 to  $\infty$  of net rate of formation terms is presented in Eq. (9) and corresponds to the 0<sup>th</sup> order moment for alkane production,  $\lambda_0^{C_nH_{2n+2}}$ , which can be calculated according to Eq. (10). Following the ASF distribution, with increasing carbon number, the corresponding species concentration tends to zero.

$$\sum_{n=5}^{\infty} R_{C_n H_{2n+2}} = R_{\lambda_0}^{C_n H_{2n+2}}$$
(9)

$$R_{\lambda_0}^{\ C_n H_{2n+2}} = \sum_{n=5}^{\infty} R_{C_n H_{2n+2}} = \sum_{n=5}^{\infty} r_{7,n}$$
(10)

Elaborating the terms in the reaction rate  $r_{7,n}$  results in Eq. (11). Substituting the summation terms for moments, the resulting expression allows to calculate the total composition of the lump of paraffins for  $n\geq 5$  in Eq. (12).

$$R_{\lambda_0}{}^{C_nH_{2n+2}} = k_{desorption} \cdot C_{H^*} \sum_{n=5}^{\infty} \left( C_{C_nH_{2n+1}^*} \right)$$

$$-k_{desorption}^{-1} \cdot C_* \cdot \sum_{n=5}^{\infty} \left( p_{C_nH_{2n+2}} \right)$$
(11)

$$R_{\lambda_0}{}^{C_n H_{2n+2}} = k_{desorption} \cdot C_{H^*} \cdot \lambda_0{}^{C_n H_{2n+1}^*}$$

$$-k_{desorption}^{-1} \cdot C_* \cdot p_{\lambda_0}{}^{C_n H_{2n+2}}$$
(12)

A similar procedure can be implemented for all moments considered. When proceeding with this methodology, it is possible to calculate the composition of methane, ethane, propane, butane and the total composition of paraffins with a total of 37 equations without losing fundamental chemical information.

#### **Results and discussions**

Figure 3 compares the CO conversion as calculated with the original model, in which the reaction network is 'truncated' at  $C_{10}$  species with the version of the model based on the moment equations. The results correspond to the PFR once steady state has been achieved. Figure 4 presents also a comparison between the two versions of the model in terms of product selectivity.



Figure 2. CO conversion. (-Truncated model. (- -) Model in terms of moment equations.



*Figure 2. CO product selectivity.* □*Truncated model* **■** *Model in terms of moment equations.* 

The performance of the two models slightly differs in conversion and product selectivity. At a similar conversion level, the truncated model seems to calculate a slightly more pronounced formation of heavier hydrocarbons. Applying the method of moments is equivalent to assuming that all hydrocarbons are included in the reaction network i.e.  $n=5 \rightarrow \infty$ .

Deviations between both versions would have been expected to be most pronounced with respect to long paraffin formation, with a lower heavier hydrocarbon production in the truncated model. However, with increasing CO conversation an inverse effect is observed. In the truncated model the formation of heavier hydrocarbons is explicitly accounted for up to  $C_{10}$ , while longer hydrocarbons are only implicitly considered in the composition of  $C_{10}$  due to end-of-chain effects. Since the formulation of the model via moment equations calculates the entire summation when  $n \rightarrow \infty$  mechanistic reasons should not be neglected to explain the differences between the two versions here studied.

# Conclusions

Accounting for 0<sup>th</sup> order moments, an alternative version of the SEMK model for the FTS has been proposed. Irrespective of the reaction network extent, a set of 37 equations allows simulating the paraffin formation through FTS. Peculiar but limited differences are obtained with the SEMK model based on the method of moments and the original, truncated network version of the SEMK model; such truncation might be the origin of the differences since the model base on the method of moments theoretically accounts for the formation of hydrocarbons when  $n \rightarrow \infty$ . Further extensions of the work will include the formation of olefins and oxygenated compounds.

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# KINETIC INVESTIGATION OF THE ANAEROBIC BIO-DIGESTION PROCESS OF ORGANIC WASTES FROM THE AGRIBUSINESS

Daniela Almeida Streitwieser<sup>a \*,</sup> and Tzu Hsin Huang<sup>a</sup>

<sup>a</sup> Universidad San Francisco de Quito USFQ, Departamento de Ingeniería Química / LaDEA

Quito D.M., Ecuador 170157

## Abstract

Biomass residues have been successfully applied for the production of second generation renewable energies. One of these applications is the anaerobic digestion of organic wastes for the production of biogas, which has already been widely studied. The microbiological reactions at each phase and the limiting step during the degradation process are well known. Also different digester designs have been developed. But further investigations need to be performed to obtain a global kinetic model necessary for the scale up and optimization of the digestion process. In this comparative kinetic study feed composition, organic load, residence time and process temperature have been systematically varied in a continuous stirred tank digester to obtain the overall kinetic parameters, necessary for the scale up into technical and industrial reactors. Also the results are compared with other macro kinetics factors, such as agitation, accessibility of the microorganism to the nutrients and biogas production yield.

The results of this study showed that biogas production depend on the feed composition, varying between high fibers and high glucose carbohydrates, as well as the content of different percentages of animal manure. But the overall kinetic parameters such as reaction order and activation energy depend only on the main sum parameters.

### Keywords

Anaerobic digestion, Organic waste co-digestion, Kinetic study.

# Introduction

The search for new energy sources has encouraged investors, researchers and costumers to look for new technologies to use the energy contained in water sources (hydro), sunlight (solar), or wind (Manzano et al, 2013). Also the residual biomass can be considered a renewable energy source, which is the organic material produced by photosynthesis. The advantage of biomass, compared to the other mentioned renewable energy sources, is that the energy contained in it can be stored, transported or transformed into gaseous, liquid or solid fuels (Saxena et al, 2009). The biomass energy can be used in thermal combustion processes or biochemical conversions. It can be distinguished between first or second generation fuels, where first generation biomass energy is obtained mainly from specialized energy crops. This energy has been widely criticized since it uses arable ground for fuel production, which can lead to food price increase, food production shortage and, in the worst scenario, hunger crisis. Therefore, second generation biomass energy is being developed and implemented all over the world. These energy sources are obtained from residues of previous agro-industrial processes or from separated municipal waste collection system (Naik, 2010). The second generation biomass not only reduces the amount of primary energy sources, but also the emission of greenhouse gases that generate from their inappropriate disposal.

The agricultural production is very important for the Ecuadorian economy. The products from the agribusiness represent 21% of the national exports, lying in second place only after the crude oil exports (BCE, 2014). The agribusiness in Ecuador represented in 2012 9.45% of the GDP (PRO Ecuador, 2014). But

\* Corresponding author: dalmeida@usfq.edu.ec

the agribusiness produces huge amounts of waste. Around 60% of the biomass produced can be considered organic wastes that need to be handled appropriately (Zhang et al, 2015).

The industrialization of the agricultural products has generated new challenges for the food industries and for the local governments, responsible for the local waste management. The huge amounts of residual biomass obtained during the processing of raw materials cannot be treated by the local waste management systems, especially because of the high organic loads and increased leaching potential.

For these reasons, an integrated solution is being designed for the internal management of the wet organic wastes produced in the agribusinesses, as a source for renewable energies. In this paper the global kinetic parameters of the anaerobic digestion process of the organic waste from fruit and vegetable processing industries will be obtained in laboratory reactors. The maximum biogas production and the kinetic parameters are obtained by controlling different operational parameters, such as composition, temperature, pH value and residence time.

#### **Materials and Methods**

#### Raw Material Selection and Inoculation

Two different sources of organic wastes from local agribusinesses are investigated. In first place the residues from the freezing process of broccoli heads, a vegetable from the cabbage family (*Brassica oleracea*), are investigated. These residues are obtained from the company *ECOFROZ S.A.* Also the residues from the fruit processing company *Latinoamericana de Jugos S.A.* are used. The main fruit wastes consists of shells, rinds, seeds and fibers of typical tropical fruits such as blackberrys (*Rubus fruticosus*), soursops (*Annona*  *muricata*), naranjillas (*Solanum quitoense*) and tree tomatoes (*Solanum betaceum*).

Both residues are being co-digested with cow manure diluted in water. The raw materials have different properties and textures, but once they are shredded and blended, their sum parameters are similar as it can be observed in Table 1.

Table 1. Sum parameters of the raw materials

Raw Material	<b>COD</b> [kg <sub>O2</sub> /m <sup>3</sup> ]	TS [%]	VS [%]	рН [-]
	50.6	12.5	10.1 ±	5.3
Fruit waste	± 4.3	± 1.6	1.4	$\pm 0.5$
Vegetable	60.1	7.72	$6.83 \pm$	5.8
waste	$\pm 4.6$	$\pm 0.8$	1.2	$\pm 1.2$
Cow	51.8	12,2	9.1 ±	6.4
manure	± 3.5	$\pm 2.3$	1.3	$\pm 1.0$

For the ramp up of the digestion process inoculum from the anaerobic digestion pilot plant from the Laboratory for Development of Alternative Energies at University San Francisco de Quito (*LaDEA*) is used. This inoculum is extracted from the reactor and injected immediately into the sealed digestion system, so that the microorganisms are not exposed to atmospheric oxygen.

The optimal relationship between the fresh raw materials: fruit or vegetable waste, and cow manure, has already been investigated by Almeida et al, (2010), and Almeida Streitwieser and Jativa (2010) using the GB<sub>21</sub> test (*Gasbildungstest*) for sludge characterization in hermetical sealed batch reactors during a period of 21 days (DIN 38414 Teil 8, 1985). The optimal ratio obtained for fruit waste / cow manure / water has been found to be 4/1/5, while for vegetable waste / cow manure/ water it is 4.5/0.5/5.

In this study the optimal organic load and the residence time in the digester need to be established. The organic load is defined as the amount of organic material fed into the reactor per volume of reactor and day, and is expressed as [kg<sub>COD</sub> /  $m^3_{reactor}$  d], where the amount of Chemical Oxygen Demand (*COD*) is calculated from the *COD* concentration of the feed multiplied by the volume of the feed.

#### Equipment

The experiments are performed with the Cole Parmer Fermentation System KH-29207-00 which is operated as a continuous stirred tank reactor. The biogas production will be obtained as a function of the organic load, which is defined as the amount of organic material fed into the reactor per reaction volume and day, expressed as  $[kg_{COD}/ m^3_{reactor}d]$ . The organic material is calculated from the *COD* concentration of the feed multiplied by the feed volume. With these results the kinetic parameters for the anaerobic digestion of the organic waste can be obtained.

The main operational parameters are measured in order to have a better control and understanding of the process. The pH value is measured by the ColeParmer autoclavable pH Probe and the Oakton 800 Series DIN pH/ORP controller and is regulated with the addition of a 1M NaOH solution. Temperature is measured by an integrated RTD and a ThermoWorks controller. The daily biogas production is obtained by the displacement of 0,05N H<sub>2</sub>SO<sub>4</sub> solution.

#### Reagents

The following reagents have been used for the characterization of the raw materials and products: NaOH (>99%) and  $H_2SO_4$  (30%) bought from *Lab. Reactivos H.V.O* (Quito). HR COD2 *Test'n Tube* Chemical Oxygen Demand reagents vials from HACH were bought from *HDM Elquitécnica*. All reagents were used in the condition they were received.

#### Characterization Methods

The characterization of the feed, the biogas and the reactive mixture are realized according to the following methods. Chemical oxygen demand (*COD*) is determined by colorimetric method within the *Test*'n *Tube* vials, based on the Hach procedures (Hach, 2007). Total solids (TS) and total volatile solids (VS) are analyzed according to the APHA (2005).

#### Experimental Approach for the Kinetic Study

The kinetic study of the anaerobic digestion has been approached by the classical potential law model. This model describes the reaction rate as a function of the concentration. In this study the reaction rate is described as the amount of organic material that has degraded into biogas ( $R_{COD;degr}$ ,  $[kg_{COD,degr}/m^3_Rd]$ ) and is a function of the concentration of organic material available in the reactor, represented as chemical oxygen demand ( $C_{COD,R}$  [ $kg_{COD}/m^3$ ]). This expression is presented in Eq. 1 and can be linearized to obtain the kinetic parameters, n and k, the reaction order and the kinetic constant, respectively.

$$R_{COD,degr} = -k \cdot C_{COD,R}^n \tag{1}$$

The degradation rate is calculated from the observed methane production by converting the daily biogas production,  $Q_{biogas}$ , with the methane content  $(x_{CH4})$  into the degradation rate of *COD*. The mass of degraded organic material  $(m_{COD,degr})$  depends on the theoretical methane production,  $Q_{CH4,theor}$ , obtained from the stoichiometric relationship of the anaerobic reaction of biomass, cellulose or glucose, into the products CH<sub>4</sub> and CO<sub>2</sub> as shown in Table 2. For the vegetable-manure mixture cellulose has been used as the primary biomass source for the reaction rate calculation according to Eq. 2. For the fruit-manure mixture equal amounts of cellulose and glucose have been assumed.

$$R_{COD,degr} = \frac{Q_{biogas} \cdot x_{CH4}}{V_R} \left[ \frac{m_{COD,degr}}{Q_{CH4,theor}} \right]$$
<sup>(2)</sup>

Where  $Q_{CH4}$  is the daily methane production [m<sup>3</sup>/d] obtained by the degradation of a defined amount of COD,  $m_{COD;degr}$ .  $V_R$  is the reaction volume.

Table 2. Anaerobic degradation of biomass

Compound	Chemical reaction	Q <sub>CH4,theor</sub> / m <sub>COD,deg</sub> [m <sup>3</sup> /kg <sub>COD</sub> ]
Glucose	$C_6H_{12}O_6 \rightarrow 3CH_4 + _3CO_2$	0.373
Cellulose	$C_5H_{10}O_6 + H_2O \rightarrow 3CH_4 + 3CO_2$	0.414

The temperature dependence of the degradation process is obtained by applying linearized Arrhenius law, where activation energy,  $E_a$ , and preexponential factor,  $k_0$ , are obtained (Levenspiel, 2005). The COD degradation rate will also be calculated by a hyperbolic model considering the Michaelis-Menten approaches in the complete manuscript and will be compared to other kinetics investigations (Siles et al, 2008) (Lin et al, 2011).

#### **Results and Discussion**

#### Evaluation of the organic load variation

First the anaerobic digestion process is stabilized at a mean temperature of 33.9±0.4 °C. The organic load is then varied systematically to obtain the biogas production as function of the organic load. The results can be observed in Figure 1 for the broccoli waste/ manure mixture (Veg-Man-Mix) and for the fruit waste/ manure mixture (Fruit-Man-Mix). It can be observed that the biogas production is over three times higher for the broccoli residue compared to the fruit waste. The percentage of methane contained in the biogas is similar in both residues within a range of 57 – 71%. The only difference during the experiments was the set point of the pH value as presented in Figure 2. In the experiments with the fruit waste a minimum pH value of 6.5 is set and small amounts of NaOH are consumed between 0 and 40 mL/d. While in the experiments with the vegetable residue, the minimum pH value is set to 7.0, which causes high consumption of of 1M NaOH of up to 160 ml/d.



Figure 1. Biogas production and methane content of the different experiments for organic load variation

In Figure 3 the COD concentration of the inlet and exit streams are presented, as well as its COD mass flow rates. It can be observed that the inlet COD concentration, as well as the inlet stream for both experiments, lie above the outlet values. This shows that COD is being degraded during the digestion process.



Figure 2. Operational parameters: alkali consumption for pH value regulation





Figure 4. Biogas and methane production, and pH values at temperature variation

#### Temperature dependence of the biogas production

The temperature dependence of the degradation process is investigated at a constant organic load of 1.5  $[kg_{COD}/m_{reactor}^3 d]$  using only the fruits waste / manure mixture. In Figure 4 the biogas and methane productions are presented. Also the pH value for the experiments can be observed ranging from 6.5 to 6.9. The NaOH consumption varies between 10 – 70 mL/d, which is in the same range as the experiments at 35°C with the same organic load.

#### Kinetic investigation

The potential law approach has been investigated to obtain the global kinetic parameters for the degradation rate of COD in the digestion process as a function of the COD concentration in the CSTR reactor. Using the logarithm base 10 the potential law expression can be linearized and the kinetic parameters: reaction order, n, and kinetic constant, k, can be obtained. In Figure 5 the linearized expressions are presented for both substrates.



Figure 5. Potential law for the organic load variation



Figure 6: Linearized Arrhenius approach

Table 3.	Resulting	kinetic	parameters
			p

Substrate	Units	Veg-	Fruit-	Mean
		Man	Man	
Reaction order, n	[-]	3.87	3.70	3.78
Kinetic const., k	[kg <sub>COD</sub> /	4.53E-5	5.90E-6	2.56E-5
Pre-exp. factor, k <sub>0</sub>	$m^{3}]^{1-n}$		1.00E+7	
Act. Ener., EA	[kJ/mol]		63.40	

Using these results to obtain an average reaction order, the kinetic constant can be calculated at different temperatures. By applying the linearized Arrhenius expression, as shown in Figure 6, the activation energy and the pre-exponential factor can be obtained. The resulting kinetic parameters are presented in Table 3.

#### Conclusions

In this study a kinetic approach for the anaerobic digestion of fruit and vegetable residues has

been performed. Both substrates have been studied for a wide range of organic loads, showing that the biogas production for the vegetable residues is over three times higher than for the fruit residues. The potential law model has been applied for the calculation of the overall kinetic parameters, resulting in a mean reaction order of 3.78. This value cannot be explained yet by a reaction mechanism, but it is useful for the design and scale up of the anaerobic digestion process. It also shows that the process rate is determined by one of the biological reactions. The pre-exponential factor and the activation energy were found to be 1.0E7 [kg<sub>COD</sub>/ m<sup>3</sup>]<sup>1-n</sup> and 63.40 [kJ/mol], which lies within the range of biological reactions. Further investigation will be performed to determine if a reaction rate change is observed at temperatures above 45°C, since the Arrhenius diagram does not show an adequate approximation with one line of the Arrhenius approach. This indicates the possibility that at this temperature already a change from the mesophilic to the thermophilic range is being observed.

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# Kinetic study of the pyrolysis and oxidation of unsaturated alcohols

R. De Bruycker<sup>a</sup>, O. Herbinet<sup>b</sup>, F. Battin-Leclerc<sup>b</sup>, K. Van Geem<sup>a,•</sup>

<sup>a</sup>Laboratory for Chemical Technology, Ghent University, Technologiepark 914, 9052 Gent, Belgium <sup>b</sup>Laboratoire Réactions et Génie des Procédés, CNRS, Université de Lorraine, 1 rue Grandville, 54000 Nancy,

France

## Abstract

Alcohols, often considered as biofuels, can form unsaturated alcohols during oxidation and pyrolysis. The reactivity of unsaturated alcohols with a C=C double bond in the  $\beta$ - and  $\gamma$ -position to the hydroxyl group is not well established, in contrast to unsaturated alcohols with a C=C double bond in the  $\alpha$ -position to the hydroxyl group, e.g. ethenol. The pyrolysis and oxidation of two such unsaturated alcohols has been studied in this work, i.e. prenol (3-methyl-2-buten-1-ol) and isoprenol (3-methyl-3-buten-1-ol). Experiments at three equivalence ratios, i.e.  $\varphi = 0.5$ ,  $\varphi = 1.0$  and  $\varphi = \infty$  (pyrolysis), were performed using a quartz isothermal jet-stirred reactor at temperatures ranging from 500 to 1100K and a pressure of 0.107 MPa. The feedstock and reaction products were quantified using gas chromatography. Isoprenol is mainly consumed by a unimolecular reaction to formaldehyde and isobutene, confirmed by quantum chemical calculations. Important products during prenol pyrolysis and oxidation are prenal (3-methyl-2-butenal) and isoprene (2-methyl-1,3-butadiene). These are formed following hydrogen abstraction from prenol.

#### Keywords

isoprenol, prenol, oxidation, pyrolysis, unimolecular reaction

#### Introduction

Alcohols with various molecular structures can be used in spark-ignition and compression-ignition engines (Sarathy et al., 2014). These fuels are generally consumed by dehydration, scission and hydrogen abstraction reactions under combustion relevant conditions.

Ethanol is the most-widely used alcohol today. Ethanol, see Figure 1(a), is an important intermediate during its oxidation and pyrolysis. Furthermore, ethenol can be formed by OH+ethene (Senosiain et al., 2006) and OH+propene (Zador et al., 2009) reactions. Ethenol can react with formation of acetaldehyde by keto-enol tautomerization, which is catalyzed by HO<sub>2</sub> radicals (da Silva et al., 2009) and carboxylic acids (da Silva, 2010) in the gas phase.



Figure 1 Molecular structures of (a) ethenol, (b) isopentanol (3-methyl-butan-1-ol), (c) isoprenol (3-methyl-3-buten-1-ol), (d) prenol (3-methyl-2-buten-1-ol)

Larger alcohols, often considered as nextgeneration biofuels, can form larger enols during oxidation and pyrolysis. The hydroxyl group can be separated from the C=C double bond by one or more carbon atoms.

For example, the radical formed following hydrogen abstraction from  $C_{\delta}$  in 3-methyl-butan-1-ol, see Figure 1(b), can decompose by C-C  $\beta$ -scission forming methyl and 3-buten-1-ol while the radical formed following hydrogen abstraction from  $C_{\beta}$  in 3-methyl-butan-1-ol, see Figure 1(b), can decompose by C-C  $\beta$ -scission forming methyl and 2-buten-1-ol.

While the reactivity of unsaturated alcohols with a C=C double bond in the  $\alpha$ -position to the hydroxyl group, especially ethenol, has already been investigated, this is not the case for unsaturated alcohols with a C=C double bond in the  $\beta$ - and  $\gamma$ -position to the hydroxyl group.

Recently, Welz et al. (2015) investigated the chlorine-atom initiated low-temperature oxidation of prenol (3-methyl-2-buten-1-ol) and isoprenol (3-methyl-3-buten-1-ol). In their experiments, chlorine atoms, which are generated from  $Cl_2$  by pulsed laser photolysis, abstract hydrogen from prenol and isoprenol. The resulting radicals react with oxygen and the product spectrum is analyzed using multiplexed synchrotron photoionization mass spectrometry. The oxidation of prenol and isoprenol mainly forms prenal + HO<sub>2</sub> (3-methyl-2-butenal) and isoprenal + HO<sub>2</sub> (3-methyl-2-butenal) and isoprenal + HO<sub>2</sub> (3-methyl-3-butenal) under their conditions (550K, 8torr), which is supported by quantum chemical calculations. Their results suggest that the presence of the C=C

<sup>•</sup> To whom all correspondence should be addressed

double bond in alcohols reduces low-temperature reactivity compared to their saturated counterpart, i.e. 3-methyl-butan-1-ol.

The objective of this study is to investigate the pyrolysis and oxidation of unsaturated alcohols where the hydroxyl group is separated from the C=C double bond by one and two carbon atoms. The oxidation and pyrolysis of prenol and isoprenol is studied in a jet-stirred reactor at atmospheric pressure and by the use of a detailed kinetic model.

# Experimental procedure

The oxidation of prenol and isoprenol was performed in a jet-stirred reactor. The followed experimental procedure is well-established and only a brief discussion will be given here. A detailed description can be found elsewhere (Herbinet et al., 2012) (Herbinet et al., 2014).

Prenol and isoprenol were purchased from Sigma-Aldrich (stated purity of 98%) while helium and oxygen were provided by Messer (purities of 99.99% and 99.999% respectively).

The flow rate of helium and oxygen was controlled using two gas-mass-flow controllers. The flow rate of the unsaturated alcohols was controlled using a liquid-mass-flow controller. This stream is evaporated by a single-pass heat exchanger and subsequently mixed with helium and oxygen.

The mixture helium/oxygen/fuel is heated to the reaction temperature in an annular pre-heating zone to avoid thermal gradient in the reactor. The residence time of the gas in this zone is negligible compared to the residence time in the jet-stirred reactor.

The mixture enters the spherical quartz reactor (volume =  $8.12 \ 10^{-5} \ m^3$ ) through four nozzles, in positions that ensure homogeneity. Both reactor and annular pre-heating zone are heated with Thermocoax resistance wire. The temperature in the reactor was kept constant and was controlled using a type K thermocouple which measures the temperature at the center of the reactor. The pressure was kept constant at 0.107 MPa using a needle valve positioned downstream of the reactor.

Three gas chromatographs were used to analyze the reactor effluent. The first gas chromatograph is connected to the reactor outlet by means of a heated transfer line. It is equipped with a thermal conductivity detector and a carbosphere packed column. It is dedicated to online quantification of O<sub>2</sub>, CO and CO<sub>2</sub>. The second gas chromatograph is also connected to the reactor outlet by means of a heated transfer line. It is equipped with a flame-ionization detector, preceded by a methanizer, and a PLOT-Q capillary column. It is dedicated to online quantification of C1-C5 hydrocarbons and small oxygenated molecules. The third gas chromatograph is equipped with a flame ionization detector and a HP-5MS capillary column. It is dedicated to quantification of C<sub>6+</sub> hydrocarbons and large oxygenated molecules.

In the case of isoprenol oxidation and pyrolysis, this GC was connected to the reactor outlet by means of a heated transfer line. A different procedure for analysis of  $C_{6+}$  hydrocarbons and large oxygenated molecules was followed during prenol oxidation and pyrolysis. Heavy species, including prenol, were condensed in a liquid nitrogen trap connected to the reactor outlet. After a known period of time, the trap was disconnected and an internal standard (*n*-octane) and solvent (acetone) were added. The content of the trap was injected on the third GC for quantification. The latter procedure is well-established and details can be found elsewhere (Herbinet et al., 2011).

Off-line analysis of the heavy fraction during prenol oxidation and pyrolysis allowed to check the carbon balance for all experiments within 5%. This was not the case during attempts with on-line analysis for the heavy fraction, possibly due to condensation/sticking of prenol on the walls of the heated transfer line.

# Kinetic model development

A preliminary kinetic model for oxidation and pyrolysis of isoprenol and prenol has been developed. It consists of two parts.

The first part is the recent mechanism by Burke et al. (2014) for propene oxidation. This mechanism, the base mechanism, contains all relevant chemistry for hydrogen, methane, ethane, ethene, propene, isobutene, methanol, ethanol and acetaldehyde oxidation.

The second part is a mechanism with reactions describing prenol and isoprenol consumption. Furthermore, this part of the kinetic model contains thermochemistry and elementary reactions for primary radicals and products, formed following prenol and isoprenol consumption, which are not included in the base mechanism. Kinetics for the unimolecular reaction of isoprenol to isobutene and formaldehyde were determined by quantum chemical calculations at the CBS-QB3 (Montgomery et al., 1999) level of theory, using the Gaussian 09 revision B suite of programs (Frisch et al., 2009). Details regarding the used methodology can be found elsewhere (De Bruycker et al., 2015). The unimolecular reaction of isoprenol to isobutene and formaldehyde is a retro-ene reaction where the hydrogen of the hydroxyl group bridges to the C=C double bond. The corresponding modified Arrhenius expression is k  $[s^{-1}] = 7.31 \ 10^5 \ T^{1.676}$ exp(17503/T). This retro-ene reaction is approximately a factor 500 faster than the retro-ene reaction of 1pentene forming propene and ethene. Other reactions that are part of the mechanism have been generated automatically using Genesys (Vandewiele et al., 2012). Genesys requires the user to define reactants and a set of reaction families with corresponding kinetics. Reaction rate coefficients for intermolecular intramolecular hydrogen abstraction and ßscission/radical addition were determined using the comprehensive group-additive framework developed at the Laboratory for Chemical Technology (Van de Vijver et al., 2015). Rate rules for the oxidation of alkyl radicals were taken from the recent work by Bugler et al. (2015). Kinetic parameters for the oxidation of resonantly stabilized radicals and  $\alpha$ hydroxyalkyl radicals have been estimated using analogy with allyl (Burke et al., 2014) and  $\alpha$ hydroxyethyl (Metcalfe et al., 2013). Thermochemistry is estimated using Bensons group additivity method (Benson, 1976).

#### **Results and discussion**

#### Isoprenol

Experiments were performed in the jet-stirred reactor with an initial isoprenol mole fraction of 0.008, diluted in He. Three equivalence were investigated, i.e.  $\phi = 0.5$ ,  $\phi = 1.0$  and  $\phi = \infty$  (pyrolysis).



Figure 2 Mole fractions as a function of temperature for isoprenol oxidation and pyrolysis in a jet-stirred reactor, P=0.107 MPa,  $F_V = 4.06 10^{-5} m^3/s$ ,  $\varphi = 0.5$ (blue),  $\varphi = 1.0$  (red) and  $\varphi = \infty$  (black) :  $\blacksquare$  - isoprenol (A),  $\bullet$  - isobutene (B),  $\bullet$  - formaldehyde (C); lines, mole fraction profiles calculated with CHEMKIN using the perfectly stirred reactor model and the kinetic model

The temperature was varied between 500 and 1100K. Approximately 40 molecules were detected and quantified.

Isobutene and formaldehyde have a very high selectivity during isoprenol oxidation and pyrolysis. In the case of  $\varphi = \infty$ , formaldehyde and isobutene mole fraction raise up to 0.008 as isoprenol gets converted. Their mole fractions remain relatively constant up to 950K, before they drop. In the case of  $\varphi = 0.5$  and  $\varphi = 1.0$ , mole fraction profiles of formaldehyde and isobutene reach a maximum of approximately 0.006 at 750K. Obviously, the presence of oxygen in the inlet stream accelerates their consumption compared to pyrolysis. Important detected oxygenated intermediates at this temperature are 2-methyl-2-propenal, 2-methyl-propanal and acetone which are known products of isobutene oxidation (Dagaut et al. 1998) (Bauge et al. 1998).

Model calculated mole fraction profiles for isoprenol are in qualitative and quantitative agreements with the experimental mole fraction profiles. Reaction path analysis shows that isoprenol is mainly consumed by the unimolecular reaction to formaldehyde and isobutene. Most other species detected in the reactor effluent are products of isobutene/formaldehyde pyrolysis/oxidation. Corresponding reactions are part of the base mechanism and not the focus of this work.

#### Prenol

Experiments with prenol were performed in the jet-stirred reactor, using similar operating conditions as isoprenol, i.e. initial mole fraction of 0.008, diluted in He,  $\varphi = 0.5$ ,  $\varphi = 1.0$  and  $\varphi = \infty$ .

In the presence of oxygen, the onset of prenol consumption is at approximately 650K, see Figure 3 (A). In pyrolysis, this temperature is shifted to approximately 950K. Approximately 50 molecules were detected and quantified in the reactor effluent. The maximum in mole fraction profiles of intermediate molecules is substantially lower compared to isobutene and formaldehyde in isoprenol oxidation and pyrolysis. The main intermediate species are prenal (3-methyl-2butenal) and isoprene (2-methyl-1,3-butadiene), see Figure 3 (B) and (C). Isoprene can be formed by hydrogen abstraction from  $C_{\delta}$  in prenol, followed by C-O \beta-scission. Prenal can be formed by hydrogen abstraction from  $C_{\alpha}$  in prenol followed by O-H β-scission or by oxidation of the resulting radical (Welz et al., 2015), see Figure 4. As the latter oxidation pathway is not possible in pyrolysis conditions, experimental prenal mole fractions are lower at  $\varphi = \infty$ compared to  $\varphi = 0.5$  and  $\varphi = 1.0$ , see Figure 3 (B). Note that both  $C_{\alpha}$  and  $C_{\delta}$  radicals are resonantly stabilized and can interconvert by intermolecular hydrogen abstraction, which proceeds through a 5membered transition state.


Figure 3 Mole fractions as a function of temperature for prenol oxidation and pyrolysis in a jet-stirred reactor, P=0.107 MPa,  $F_V = 4.06 \ 10^{-5} m^3/s$ ,  $\varphi = 0.5$ (blue),  $\varphi = 1.0$  (red) and  $\varphi = \infty$  (black) :  $\blacksquare$  - prenol (A),  $\bullet$  - prenal (B),  $\bullet$  - isoprene (C); lines, mole fraction profiles calculated with CHEMKIN using the perfectly stirred reactor model and the kinetic model

As can be observed from Figure 3, the model calculated conversion profiles have a higher gradient than the experimental conversion profiles and are shifted to higher temperatures. This has a negative impact on the model performance regarding prenal and isoprene. Clearly, some low temperature reaction pathways are missing or related kinetic and thermodynamic data need to be reevaluated.



Figure 4 Main reaction paths following hydrogen abstraction from prenol

### Conclusions

Unsaturated alcohols are important intermediates during the oxidation and pyrolysis of saturated alcohols, proposed biofuels. In this work, the oxidation and pyrolysis of two unsaturated alcohols, prenol and isoprenol, has been investigated in a jetstirred reactor at temperatures below 1100K and quasiatmospheric pressure.

Isoprenol oxidation and pyrolysis have a very high selectivity to formaldehyde and isobutene at low temperatures. This is confirmed by quantum chemical calculations regarding the retro-ene reaction of isoprenol to the aforementioned products. At higher temperatures, the observed product spectrum resembles that of isobutene/formaldehyde oxidation/pyrolysis.

Prenol pyrolysis and oxidation appears to be dominated by radical chemistry. Isoprene and prenal are the main observed intermediate species. Both molecules can be formed by hydrogen abstraction from prenol, which leads to resonantly stabilized radicals, followed by  $\beta$ -scission, oxidation reactions. The preliminary automatically-generated model is currently incapable of accurately reproducing the observed conversion profiles.

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# **REACTION OF CH3 RADICALS WITH HO2**

Chao Yan<sup>\*</sup>and Lev N Krasnoperov New Jersey Institute of Technology Newark, NJ 07102

# Keywords

Hydroperoxy radicals, Methyl radicals, Gas kinetic, Combustion.

Reaction of methyl radicals with hydroperoxy radicals (1) plays a very important role in hydrocarbon combustion. One of the important channels of this reaction (1a) converts a relatively inert  $HO_2$  radical to very reactive methoxy and hydroxyl radicals, therefore converting a fraction of chain termination into chain propagation:

CH<sub>3</sub>  $HO_2$  $\rightarrow$  $CH_3O +$ + OH  $\rightarrow$  $CH_4$  $O_2$ +Kinetic studies of reaction 1 are difficult, due to the lack of direct photolytical sourses of HO<sub>2</sub> radicals as well as thermal instability of some traditional precursors of the radical (such as  $H_2O_2$ ). Untill recently, there have been no direct studies of reaction 1, current data is sparce (Fig.1).

In this work, we explored a different chemical system to simultaneously generate methyl and hydroperoxy radicals, where no compounds with weak chemical bonds are employed. Methyl radicals are produced directly in photolysis of acetone at 193.3 nm (ArF excimer laser). The photolysis system is gaseous



(1a)

(1b)

mixture of acetone/oxalyl chloride/methanol/oxygen/helium. Hydroperoxy radicals are produced in a sequence of very fast reactions initiated by chlorine

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atoms, produce	ed in ph	otolysis of oxalyl c	hloride:				
$(CH_3)_2CO$	+	hv(193.3 nm)	$\rightarrow$	2 CH3	+	CO	(2)
(COCl) <sub>2</sub>	+	hv(193.3 nm)	$\rightarrow$	2 Cl	+	2 CO	(3)
Cl	+	CH <sub>3</sub> OH	$\rightarrow$	CH <sub>2</sub> OH	+	HCl	(4)
CH <sub>2</sub> OH	+	$O_2$	$\rightarrow$	HO <sub>2</sub>	+	H <sub>2</sub> CO	(5)

Kinetics of methyl radicals is monitored via absorption at 216.4 nm.

Preliminary results at two temperatures (296 and 414 K, 1 bar, He) are show in Figure 1 (stars), together with the results of other experimental (symbols) and theoretical (lines) studies. The results indicate negative temperature dependence, in accord with the theory. Extention of the study to higher temperatures (up to 834 K) as well as pressures (up to 100 bar) is in progress.

# DEVELOPMENT OF A JOINT HYDROGEN AND SYNGAS COMBUSTION MECHANISM BASED ON AN OPTIMIZATION APPROACH

Tamás Varga<sup>1,2</sup>, Carsten Olm<sup>1,2</sup>, István Gy. Zsély<sup>1,2</sup>, Tibor Nagy<sup>1,3</sup>, Éva Valkó<sup>1,2</sup>,

Róbert Pálvölgyi<sup>1</sup>, Henry J. Curran<sup>4</sup> and Tamás Turányi<sup>1,\*</sup>

<sup>1</sup> Laboratory for Chemical Kinetics, Eötvös University (ELTE) – Budapest, Hungary

<sup>2</sup> MTA-ELTE Research Group on Complex Chemical Systems – Budapest, Hungary

<sup>3</sup> IMEC, RCNS, Hungarian Academy of Sciences – Budapest, Hungary

<sup>4</sup> Combustion Chemistry Centre, National University of Ireland Galway (NUIG) – Galway, Ireland

## Abstract

An optimized joint hydrogen and syngas combustion mechanism has been developed using a large set of indirect experimental data, consisting of ignition measurements in shock tubes and rapid compression machines, flame velocity measurements, and species profiles measured in flow reactors and jet-stirred reactors, covering wide ranges of temperature, pressure, equivalence ratio and  $H_2/CO$  ratio. The Arrhenius parameters *A*, *n*, and *E* of 18 elementary reaction steps were fitted within their domain of uncertainty, which had been determined based on direct measurements and theory. Also, 5 third-body collision efficiency factors of three reaction steps were optimized. Rate coefficient values obtained in direct measurements for these elementary reactions were also collected and included in the optimization. The joint covariance matrix of the optimized parameters characterizes the temperaturedependent posterior uncertainty domain of the optimized rate coefficients and also their correlations. The performance of the optimized mechanism was tested against 18 recent hydrogen and syngas combustion mechanisms and was found to be the most accurate one when considering all kinds of measurements.

### Keywords

combustion modeling, parameter optimization, uncertainty estimation

# Introduction

Several hydrogen and syngas combustion mechanisms were published in the last years; see e.g. the reviews of Davis et al. (2005), Sun et al. (2007), Li et al. (2007) and Kéromnès et al. (2013). In most of these mechanisms the majority of the parameters were based on directly measured or theoretically calculated rate coefficients, but also some of the rate parameters were tuned to improve the agreement with measured ignition delay times (IDTs), flame velocities or concentration profile measurements. A smaller number of recently published mechanisms were developed using optimization techniques, such as the Davis et al. (2005), You et al. (2012) and the Li et al. (2015) mechanisms.

The recent study of Olm et al. (2015) on the modelling of syngas combustion clearly showed, that while there has been a large improvement in the recent years in the description of syngas combustion, even the most recent models are not able to provide a good reproduction of all types of experimental data from indirect measurements (e.g. ignition delays, laminar burning velocities and concentration-time profiles) in the whole range of experimental conditions that has been covered in the literature.

In this work we utilized our recently developed optimization methodology to develop an improved syngas and hydrogen combustion mechanism that provides an accurate reproduction of the available experimental data on both syngas and hydrogen combustion at all experimental conditions. The optimization was based on the comprehensive collection of experimental data of Olm et al. (2014, 2015), which was extended with more recent experimental results.

The most important reactions at the conditions of the experiments were identified by sensitivity analysis, and direct rate coefficient measurements of these important reactions were also collected and utilized as optimization targets.

# The initial mechanism

We have selected the syngas combustion model of Kéromnès et al. (2013) as the starting point of our development. According to Olm et al. (2015), the mechanism of Kéromnès et al. provides one of the best overall descriptions of the indirect measurement data for both syngas and hydrogen combustion. The hydrogen combustion sub-mechanism was updated with the results obtained in our recent optimization study on hydrogen combustion (Varga et al., 2015).

The parametrization of the pressure dependence of reaction HCO + M = H + CO + M was updated based on the theoretical study of Yang et al. (2013). This reaction was handled by Kéromnès et al. as a second-order reaction at all pressures. Yang *et al.* provided a Troe-fit and high-pressure limit for the rate coefficient of the reaction, which was used with the original rate expression of Kéromnès et al. serving as the low-pressure limit.

#### The experimental data utilized

A large set of indirect experimental data relevant both to hydrogen and syngas combustion was collected and used for the development of the joint combustion mechanism. For both hydrogen and syngas combustion, all data that were used in the modelling studies of Olm et al. (2014, 2015) and during the development of our optimized hydrogen combustion mechanism (Varga et al., 2015) were also used here. Also, new experimental data were added from Hashemi et al. (2015).

Some of these data were not used as optimization targets for various reasons. Those experimental results that were identified as contradictory with all other experiments by Olm et al. were omitted. Most shock tube experiments which were conducted below 1000 K temperature behind the reflected shock wave were also omitted due to large influence of facility effects, unless this effect was characterized by the authors of the respective experiments.

Also, it has been noted by Burke et al. (2012) that speciated flame measurements could not be used well for optimization, since all simulation results are far more sensitive to the temperature profile used for the simulations than to the kinetic parameters. Therefore, such measurements were also not used in our present work.

### Selection of parameters for optimization

Local sensitivity analysis at the conditions of the indirect experimental data was carried out based on the initial mechanism. Sensitivity coefficients were calculated for each of the collected experimental results, with respect to the A-factors of each reaction, including A-factors describing the low-pressure limit rate coefficients for the fall-off reactions. The sensitivity coefficients of third-body collision efficiencies were also calculated.

The list of the rate parameters chosen for optimization is given in Table 1. Altogether, 48 Arrhenius parameters of 18 reactions and 5 third-body collision efficiencies were optimized. A collection of direct rate coefficient measurements was carried out for the selected reactions. Altogether 2275 datapoints in 85 datasets were used. The number of direct measurements used for each reaction step is given in Table 1.

### **Optimization methodology**

We have applied our previously described global parameter optimization method (Turányi et al., 2012) to our collected indirect and direct experimental data to determine the optimal value of the Arrhenius parameters and third-body collision efficiencies. The optimal set of parameters was achieved by the minimization of the following objective function:

$$E(\mathbf{p}) = \frac{1}{N} \sum_{i=1}^{N} \frac{1}{N_i} \sum_{j=1}^{N_i} \left( \frac{Y_{ij}^{\text{mod}}(\mathbf{p}) - Y_{ij}^{\text{exp}}}{\sigma(Y_{ij}^{\text{exp}})} \right)^2$$
(1)

Here *N* is the total number of datasets used as optimizations targets,  $N_i$  is the number of datapoints in the *i*th dataset,  $Y_{ij}^{\text{mod}}$  and  $Y_{ij}^{\text{exp}}$  are the modelled and experimental results for the *j*-th point of the *i*-th dataset, respectively, and  $\sigma(Y_{ij}^{\text{exp}})$  is the 1 standard deviation experimental error assigned to the datapoint.

As part of our method, a global minimum search of the above error function is carried out. Such global parameter optimization methods require a definition of a domain of the parameters in which the optimum is sought, because searching for the optimal parameter set would be impossible in an unbounded parameter space. Nagy et al. (2015) have published temperature-dependent uncertainty domains for all of the reactions selected for optimization in present work and these were used as the prior uncertainty domains for these rate coefficients.

### **Results and discussion**

As a result of the optimization, the error function was significantly decreased, and a model better describing the collected indirect and direct experimental measurement data was developed. Optimal values were obtained for the 53 rate parameters, and their covariance matrix was estimated using the method described by Turányi et al. (2012). From the covariance matrix of the rate parameters, temperaturedependent uncertainty ranges were obtained for the rate coefficients of each optimized reaction.

The performance of the optimized mechanism was compared to several hydrogen and syngas combustion mechanisms that have been validated or extensively used for the simulation of hydrogen and syngas combustion.

Table 2 contains the calculated error function values for the best mechanisms for syngas combustion data, also given separately for experimental categories (ignition delays, laminar burning velocities and concentration profiles). In several measurements of the flame velocity, helium was used as the bath gas or a component of the diluent mixture. Only mechanisms that have assigned third-body collision efficiency values for helium to the pressure-dependent reactions are presented in the current comparison.

		Direct measurements		Optimized parameters		
	Optimized subset of reactions		Datasets	lnA	n	E/R
R1	$H + O_2 = O + OH$	745	9	36.16	-0.4859	8116
R2	$O + H_2 = H + OH$	338	11	14.04	2.270	3501
R3	$OH + H_2 = H + H_2O$	181	7	16.40	1.878	1586
R4	$OH + OH = O + H_2O$	173	4	11.35	2.2642	-898.2
R5	$H + H + M = H_2 + M$	2	1	43.05	-1.213	308.0
R8	$H + OH + M = H_2O + M$	6	3	55.66	-2.538	60.79
R9	$\mathbf{H} + \mathbf{O}_2 + \mathbf{M} = \mathbf{H}\mathbf{O}_2 + \mathbf{M}$	149	10	45.41	-1.373	-
R10	$H + HO_2 = H2 + O_2$	10	1	14.57	2.113	-817.7
R11	$HO_2 + H = OH + OH$	-	-	31.69	-	86.07
R13	$HO_2 + OH = H_2O + O_2$	67	4	27.59	0.4201	-477.4
R15	$HO_2 + HO_2 = H_2O_2 + O_2$	73	4	35.01	-	7826
R16	$OH + OH + M = H_2O_2 + M$	113	6	42.14	-1.178	-2150
R18	$H_2O_2 + H = H_2 + HO_2$	4	1	46.03	-1.925	4743
R23	$\mathrm{CO} + \mathrm{O}_2 = \mathrm{CO}_2 + \mathrm{O}$	39	1	28.69	-	24005
R24	$CO + OH = CO_2 + H$	205	15	9.717	2.221	-694.7
R26	HCO + M = H + CO + M	170	8	24.62	0.9596	7368
R28	$HCO + H = CO + H_2$	-	-	31.79	-	-

Table 1. The optimized reactions with the respective number of utilized direct rate coefficient measurements, and the values of the optimized Arrhenius-parameters. Units are mol  $cm^3 K s$ .

Optimized third-body collision efficiencies: reaction R8: m(He)=0.44; reaction R9:  $m(\text{H}_2)=1.51$ , m(Ar)=0.474,  $m(\text{H}_2\text{O})=11.37$ ; R26: m(Ar)=0.79



Figure 1. The Arrhenius plots of the initial and the optimized rate coefficients of reactions R24 and R13. The thin solid and dotted lines denote the initial rate coefficients and their domain of uncertainty, respectively, and the thick solid line and dashed lines denote the optimized rate coefficients and their domain of uncertainty, respectively.

Table 2. The average error function values for indirect measurements relevant to syngas combustionby experiment type, for the best mechanisms.

		Meas	ured data (No	). of datasets/p	oints)
Mechanism	Reference	IDT (94/938)	Conc (37/777)	Flame vel. (194/1879)	Total (325/3594)
ELTE Syngas 2015	This work	14.83	7.95	4.84	8.08
NUIG NGM 2010	Healy et al. (2010)	26.52	11.72	7.84	13.69
Kéromnès 2013	Kéromnès et al. (2013)	38.09	21.34	6.29	17.20
Davis 2005	Davis et al. (2005)	52.04	13.49	4.36	19.19
POLIMI 2014	CRECK modeling group (2014)	45.28	29.17	5.89	19.93
Li 2015	Li et al. (2015)	19.80	105.73	5.92	21.30

The results show that the present optimized model provides the best reproduction of syngas combustion data. It is either the best or among the best performing mechanisms for each experiment type. For the hydrogen combustion subset, a very similar overall performance was obtained as with our previously published, optimized hydrogen combustion mechanism (Varga et al., 2015). The obtained error function values were only slightly higher than in the case of our optimized hydrogen mechanism which indicates that only a small degree of inconsistency exists between the collected hydrogen and syngas combustion data.

Figure 1 shows examples of the optimized rate coefficients and their  $3\sigma$  uncertainty limits. The rate coefficients of all reactions could be determined with significantly smaller uncertainty than the prior uncertainties as determined by Nagy et al. (2015), with the exception of reaction R28 (HCO + H = CO + H<sub>2</sub>) where the determined uncertainties were slightly larger than the values of Nagy et al (2015).

#### Conclusions

An accurate joint hydrogen and syngas combustion mechanism was developed using an optimization approach. A comprehensive set of experimental data, both indirect and direct, were used as optimization targets. A significant overall improvement was achieved in the description of the syngas combustion data compared to all of the investigated syngas mechanisms, and a similarly good overall performance was achieved for hydrogen combustion as in our previous optimization study (Varga et al., 2015). The optimized mechanism provides realistic results in the ranges of the validation, and it is a good candidate for a base mechanism for the development of larger combustion mechanisms and automatic mechanism generation.

The covariance matrix of the optimized parameters was calculated and temperature-dependent uncertainty ranges of the rate-coefficients were obtained for each of the optimized reactions. Almost all rate coefficients could be determined with small (posterior) uncertainty and we consider the optimized values as our currently best recommendations for the physical values of the rate coefficients.

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# ENERGY DIAGRAMS OF OOQOOH AND DETAILED CHEMICAL KINETICS MODELING ON THE LOW-TEMPERATURE OXIDATION OF DIETHYETHER

Yasuyuki Sakai<sup>1</sup>, Shinichiro Tsukatani<sup>1</sup>, Motohiro Oshima<sup>2</sup>, Mustapha Fikri<sup>3</sup> and Ravi X Fernandes<sup>4</sup> <sup>1</sup>Department of Mechanical Engineering, University of Fukui, 9108507 Fukui, Japan <sup>2</sup>Department of Mechanical Systems Engineering, Toyama Prefectural University, 9390398 Toyama, Japan <sup>3</sup>Institute for Combustion and Gas Dynamics – Reactive Fluids, University of Duisburg-Essen, 47048 Duisburg, Germany

<sup>4</sup>Physikalisch-Technische Bundesanstalt, Braunschweig, Germany D38116

### Abstract

A detailed chemical kinetic model has been developed to elucidate the auto-ignition behavior of diethylether in internal combustion engines. The high-temperature oxidation and C0-C2 base mechanism were assembled from the literature. For the low-temperature oxidation species, the reactions of ROO and QOOH radicals were studied in our earlier theoretical study with quantum chemical and transition state theory approach. In the present study, the potential energy surfaces for the unimolecular reactions of OOQOOH isomers have been obtained by using a CBS-QB3 composite method. It was found that the reaction barriers of the hydrogen shifts from  $\beta$  carbon (terminal carbon) with OOH group decrease as in the alkane oxidation, on the other hand, there is no effect of OOH group for the hydrogen shifts from  $\alpha$  carbon (next to ether group), thus, the reaction barriers of OOQOOH isomers have same trend with corresponding ROO radical. This fact leads to the estimation for the reactions of OOQOOH isomers. The constructed model was validated against the ignition delay times of DEE/O<sub>2</sub>/Ar mixtures provided in the literature, and it reproduces well at temperatures of 940-1300 K and pressures of 1.0 and 2.0 MPa, although, the model overpredicts the experimental data at 4.0 MPa.

### Keywords

Diethylether, Modeling, Low-Temperature Oxidation, Second-O2 addition, Potential Energy Surface

### Introduction

Diethyl ether (DEE) has an exceptional cetane number compared to other conventional gasoline and diesel fuel components. In order to utilize this promising property in optimizing fuel blends for internal combustion engines, detailed knowledge on the chemical kinetics of DEE oxidation, especially under engine relevant temperatures and pressures, is desired. The pyrolysis and oxidation of DEE have been studied by using shock tube techniques (Yasunaga, et al., 2010). A detailed chemical kinetic model was proposed and validated against these measurements. This model can reproduce the measured species data and ignition delay times at temperatures from 900 to 1900 K and pressures from 0.1 to 0.4 MPa. Recently, ignition delay times of DEE were measured in shock tube and rapid compression machine (Werler, et al., 2014). These measurements covers at temperatures from 500 to 1300 K and pressures from 0.25 to 4 MPa. They showed that the hydrogen atom abstraction of fuel by HO<sub>2</sub> radical have an impact on the predictions of chemical kinetic model developed by Yasunaga. Zhang et al. also measured ignition delay times behind the reflected shock waves at temperatures from 1050 to 1600 K and

> Corresponding author; Yasuyuki Sakai (Email to y\_sakai@u-fukui.ac.jp)



Figure 1. Species abbreviations and their chemical structure.

pressures of 0.12, 0.4, and 1.6 MPa (Zhang, et al., 2015). They analyzed the ignition mechanism of DEE by using a chemical kinetic model under their experiment conditions.

For the comprehensive understanding of DEE oxidations in internal combustion engines, the low-temperature oxidation mechanism must be investigated by both experimentally and theoretically. Our earlier theoretical study reported the energy diagrams and high-pressure rate constants of 1 and 2-ethoxyethylperoxy radicals, which are important

intermediates in the low-temperature oxidation of DEE (Sakai, et al., 2015). In the present study, the energy diagrams of all OOQOOH isomers, identified in the sub-mechanism of DEE oxidations, have been investigated by using a quantum chemical method. Based both energy diagrams obtained in this study and our earlier theoretical study, a detailed chemical kinetic model with low-temperature oxidation mechanism has been developed and validated against the measurements of ignition delay time available in the literature

# **Computational Method**

All quantum chemical calculations were performed by using the Gaussian 09 software package (Frisch, et al. 2004). Geometries, vibrational frequencies, and energies of reactants, products, and transition states were calculated according to the procedure of the CBS-QB3 method (Montgomery, et al., 1999 and 2000). All the stationary points were confirmed by one imaginary frequency for transition states and all positive frequencies for local minima. Ignition delay times were calculated by using the CHEMKIN-PRO package (Reaction Design, 2009). All calculations were assumed as adiabatic constant volume conditions.

 Table 1. Reaction barriers<sup>a</sup> for OOQOOH isomers and comparison with ROO isomers.

mantion		species <sup>c</sup>		
reaction	βOOQOOHp	γOOQOOHs	δOOQOOHp	$sROO^d$
13hs	154 (+1)	163 (+8)	160 (+5)	155
14hs	128 (-23)	156 (+5)	156 (+5)	151
15hs	77 (+4)	77 (+4)	80 (+7)	73
16hs	106 (+7)	123 (+24)	81 (-17)	99
ho2	131 (+4)	133 (+6)	132 (+5)	127
ooh	74	-	76	-
roaction <sup>b</sup>		species <sup>c</sup>		
reaction <sup>b</sup>	βOOQOOHs	species <sup>c</sup> δOOQOOHs	εOOQOOHp	pROO <sup>d</sup>
reaction <sup>b</sup>	βOOQOOHs 177 (+2)	species <sup>c</sup> δOOQOOHs 178 (+3)	εOOQOOHp 179 (+4)	pROO <sup>d</sup>
reaction <sup>b</sup> 13hs 14hs	βOOQOOHs 177 (+2) 113 (-2)	species <sup>c</sup> δΟΟQΟΟΗs 178 (+3) 124 (+9)	εΟΟQΟΟΗp 179 (+4) 120 (+5)	pROO <sup>d</sup> 175 115
reaction <sup>b</sup> 13hs 14hs 16hs	βOOQOOHs 177 (+2) 113 (-2) 81 (+4)	species <sup>c</sup> δΟΟQΟΟΗs 178 (+3) 124 (+9) 82 (+5)	εOOQOOHp 179 (+4) 120 (+5) 85 (+8)	pROO <sup>d</sup> 175 115 77
reaction <sup>b</sup> 13hs 14hs 16hs 17hs	βOOQOOHs 177 (+2) 113 (-2) 81 (+4) 100 (-3)	species <sup>c</sup> δΟΟQΟΟΗs 178 (+3) 124 (+9) 82 (+5) 131 (+28)	εOOQOOHp 179 (+4) 120 (+5) 85 (+8) 85 (-18)	pROO <sup>d</sup> 175 115 77 103
reaction <sup>b</sup> 13hs 14hs 16hs 17hs ho2	βOOQOOHs 177 (+2) 113 (-2) 81 (+4) 100 (-3) 154 (+19)	species <sup>c</sup> δOOQOOHs 178 (+3) 124 (+9) 82 (+5) 131 (+28) 137 (+2)	εOOQOOHp 179 (+4) 120 (+5) 85 (+8) 85 (-18) 140 (+5)	pROO <sup>d</sup> 175 115 77 103 135
reaction <sup>b</sup> 13hs 14hs 16hs 17hs ho2 ooh	βOOQOOHs 177 (+2) 113 (-2) 81 (+4) 100 (-3) 154 (+19) 76	species <sup>c</sup> δOOQOOHs 178 (+3) 124 (+9) 82 (+5) 131 (+28) 137 (+2) 79	εOOQOOHp 179 (+4) 120 (+5) 85 (+8) 85 (-18) 140 (+5) -	pROO <sup>d</sup> 175 115 77 103 135 –

<sup>b</sup> Abbreviations for the reactions are see in text.

<sup>c</sup> Species abbreviations are defined in the figure 1.

<sup>*d*</sup> Reference X.



Figure 2. Estimated rate constants, based on the reaction barrier in table1, for the reactions of OOQOOH isomers. The rate constants were taken from the reference X and X. 1Xhs, ho2, and ooh denote 1-X intramolecular hydrogen shift, concerted HO<sub>2</sub> elimination, and intramolecular hydrogen shift from hydroperoxy group to radical centered oxygen atom in peroxy group respectively.



Figure 3. Reactions of OOQOOH isomers included in the detailed chemical kinetic model for the oxidation of diethylether. The abbreviations with underline denotes the type of reactions, refer to the figure 2.

### **Estimation for the Reactions of OOQOOH**

Table 1 shows the reaction barriers for the unimolecular reactions of OOQOOH isomers. Intramolecular hydrogen shift reactions are abbreviated as 1Xhs for the 1,X-hydrogen shift and ooh for the hydrogen shift from hydroperoxy group to peroxy group. Concerted HO<sub>2</sub> elimination reaction is expressed as ho2. We have also investigated the cyclization reactions between radical centered oxygen atom and lone pair in oxygen atom included in ether and hydroperoxy group. However, these reactions have higher reaction barrier than the other reactions. Thus, we have no discussion further. In the table 1, the reaction barrier of ROO isomers also shown for the comparison purpose. It was found that the hydrogen shift reactions from carbon atom (1Xhs) have the same reaction barrier with those of pROO and sROO, when considered the estimation error reported in CBSQB3 method, around +6 kJ/mol, (Montgomery, et al., 1999 and 2000). 14hs in βOOQOOHp, 16hs in δOOQOOHp, and 17hs in EOOQOOHp have the lower reaction barrier than those of pROO and sROO. These reactions

are hydrogen shift from terminal carbon atom with OOH group. This fact was also reported in the study of low-temperature oxidation for alkanes (Miyoshi, 2011). There are exceptions from above discussions, 16hs in  $\gamma$ OOQOOHs and 17hs in  $\delta$ OOQOOHs. These two reactions have higher reaction barrier than pROO and sROO, and, shown in figure 2, are minor reaction channel if we assume the same rate constants with pROO and sROO. Concerted HO<sub>2</sub> reactions (ho2) have the same reaction barrier with pROO and sROO, although BOOQOOHs has higher reaction barrier. These reactions are minor role in the oxidation of OOQOOH, later shown in figure 2. Hydrogen shift from OOH (ooh) has the lowest reaction barrier among all reaction channels. This reaction produces the other OOOOOH isomers, and also reported in the alkane study (Miyoshi, 2011). From these calculated reaction barriers, the rate constants of OOQOOH isomers are expected to be the same value of pROO, sROO, and OOQOOH in alkane oxidations.

Figure 2 shows the estimated rate constants for the reactions of each OOQOOH isomers. Based on the discussion above, these rate constants were taken from the studies of pROO and sROO (Sakai, et al., 2015), and OOQOOH in alkane oxidations (Miyoshi, 2011). For the reactions of 16hs in yOOQOOHs, 17hs in  $\delta$ OOQOOHs, and ho2 in  $\beta$ OOQOOHs, which considered as exceptions, the rate constants were assumed as the same values of pROO and sROO. In fact, the reaction barrier of these three reactions are larger than those of pROO and sROO, the rate constants are expected smaller than the values in figure 2. From the figure 2, we concluded that these three reactions are minor channel, thus further calculations for rate constant estimation, were not performed. It was found that 15hs, 16hs, and ooh are major reaction channels for each OOQOOH isomers, if they are available. Figure 3 shows the reaction pathways of each OOQOOH isomers, based on the present results. The rate constants of the products of OOQOOH were also estimated from the rate constants of corresponding OOOH isomers (Sakai, et al., 2015). We assumed the reaction as B-fission reaction for radical species, and O-O bond fission for molecular products with OOH group.

# Modeling

The starting model was adopted from a detailed chemical kinetic model of n-pentane generated by using a KUCRS program (Miyoshi, 2011). First, the species and elementary reactions were modified with replacing the methylene group ( $-CH_2-$ ) into ether group (-O-) in the chemical structure. The rate constants for the hydrogen abstraction reactions from  $\alpha$  carbon in the fuel molecule were changed into those for alcohol fuels included in the KUCRS program as rate rules. The rate constants and thermodynamic properties of pROO and sROO were taken from our previous theoretical study (Sakai, et al., 2015). The reactions of each OOQOOH isomers and product radicals and molecular species were shown in figure 3. The present model includes 133 species and 483 reactions. Figure 4



Figure 4. Ignition delay times for the stoichiometric mixture of diethylether diluted in oxygen/argon (0.68% diethylether, 4.018% oxygen, 95.284 argon). The symbols are experimental date measured by shock tube in the reference Werler et al., 2015. The lines are simulated values of present work.

shows the comparisons between measured (Werler, et al., 2015) and calculated ignition delay times for stoichiometric DEE/O<sub>2</sub> mixture diluted in argon. The present model well reproduces the ignition delay time at temperatures of 940-1300 K and pressures of 1.0 and 2.0 MPa, although the temperature dependence of ignition delay times were differ from experimental values at 4.0 MPa.

### Conclusions

A detailed chemical kinetic model for the oxidation of DEE has been developed with combining the quantum chemical and chemical kinetic investigations on the reactions of ROO, QOOH,  $O_2QOOH$  isomers, which are critical species for the ignition under engine relevant conditions. The constructed model was validated against the ignition delay times measured in the shock tube, given in the literature. It was confirmed that the model well reproduces the experimental data at temperatures of 940-1300 K and pressures of 1.0 and 2.0 MPa.

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# DETAILED CHEMICAL KINETIC MODELING STUDY OF ISOBUTENE OXIDATION: IGNITION DELAY TIME

Chong-Wen Zhou, Yang Li, Eoin O'Connor, Henry J. Curran

Combustion Chemistry Centre, National University of Ireland Galway, Ireland

# Abstract

A detailed chemical kinetic mechanism of isobutene oxidation has been developed to describe the combustion of isobutene. Ignition delay time (IDT) experiments have also been carried out to improve our understanding of the ignition characteristic of isobutene. A series of IDT experiments were performed in NUIG shock tubes and rapid compression machines (RCMs) under conditions not previously studied. The combination of shock tube and RCM data greatly expands the data available for validation of isobutene oxidation models to higher pressures (10–50 atm) and lower temperatures (700–1500 K). Important reactions highlighted via flux and sensitivity analyses include: hydrogen atom abstraction from isobutene by molecular oxygen, hydroxyl, and hydroperoxyl radicals; methyl allyl-methyl allyl radical recombination and the reaction between methyl allyl and hydroperoxyl radicals. The current mechanism accurately predicts the combustion characteristics of isobutene across the range of experimental conditions presented in this study.

### Keywords

Isobutene oxidation, Shock tube, Rapid compression machine, Chemical kinetics, Ignition, Flame speed

### Introduction

Understanding the combustion chemistry of the butene isomers is a prerequisite for a comprehensive description of the chemistry of C1 to C4 hydrocarbon and oxygenated fuels such as butanol. For the development and validation of combustion models, it is thus crucial to improve the knowledge about the C4 combustion chemistry in detail. Isobutene, one of the butene isomers, is an important intermediate in the combustion of larger branched hydrocarbons, such as isobutene, iso-octane etc. Developing the comprehensive kinetic model of isobutene is part of our whole project in describing the C1 to C4 chemistry also an extending work based on propene<sup>1,2</sup>.

Several studies have been devoted to the pyrolysis and oxidation of isobutene<sup>3-5</sup>, there is a lack of experimental data available in the literature for isobutene at low temperatures (600–1000 K) and high pressures (>10 atm). Experiments carried out in this work are shown in Table 1.

Table1. Ignition delay time data for isobutene oxidation obtained in this study.

Reactor Type	T–Range, K	P–Range, atm	Ø Range	Dilution
Shock tube	940-1500	10-50	0.3–2.0	in "air"
RCM	700–996	10-50	0.3–2.0	in "air"

### **Experimental methods**

Ignition delay time measurements for isobutene were obtained in at NUIG ST and NUIG RCM respectively. Detailed explanation for these two facilities can be found in reference 2.

### **Partial results**

As shown in Figure 1, the current model predicts the combustion characteristic of isobutene accurately.



Figure 1. IDT validation of the model (solid and dashed lines) against the experimental results at  $\phi = 0.3$  in air.

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# High Temperature Kinetic Mechanism Development of 2-Phenyl Ethanol Combustion from Ignition Delay Time Measurements in a Shock Tube

Vijai S.B. Shankar<sup>\*1</sup>, Mohammed Al-Abbad<sup>1</sup>, Samah Y. Mohamed<sup>1</sup>, Mariam El-Rachidi<sup>1</sup>, Mohamed Beshir<sup>1</sup>, Khalil Djebbi<sup>2</sup>, Zhandong Wang<sup>1</sup>, Aamir Farooq<sup>1</sup>, and Mani Sarathy<sup>1</sup>

<sup>1</sup>Clean Combustion Research Centre, King Abdullah University of Science and Technology,

Thuwal, KSA

<sup>2</sup>École nationale supérieure d'ingénieurs de Tunis, Tunisia

# Abstract

This work focuses on combustion characteristics of a novel octane booster, 2-Phenylethnaol (2-PE), through the study of its behavior in an engine and a high pressure shock tube. The knock response of a FACE G (Fuels for Advanced Combustion Engines) gasoline with advance in spark timing was compared to two mixtures - 1. FACE G + 20% Ethanol and 2. FACE G + 20% 2-PE. The measurements covered fuel lean (0.5) and stoichiometric fuel/oxygen mixtures diluted in argon, at pressures of 10 and 20 bar and temperatures from 1075 K to 1520 K. A chemical kinetic model is also being developed with an aim to reproduce ignition delay times measured in the shock tube. The reaction classes in the 2-PE sub-mechanism were adopted from a well validated butanol mechanism (Sarathy et al., 2012) and the rates of these reactions are presently under consideration. Further reactions and rates involving products formed in the sub-mechanism were covered in the n-butyl benzene mechanism developed by (Diévart and Dagaut, 2011). The chemistry of C0-C4 species was integrated in the model through ARAMCO MECH 1.4 (Burke et al., 2014).

### Keywords

Octane Number, Knocking, Kinetic Model,

# 1. Introduction

Climate change has become the biggest challenge of our times. The consensus among climate scientists point towards Anthropogenic Global Warming (AGW) due to ever increasing concentration of Green House Gases (GHG) in the atmosphere as the main cause(Oreskes, 2004; Cook et al., 2013) even though there is a large disagreement in quantifying its effect on the environment. While science is not a democracy, the multitude of growing evidence cannot be ignored. The National Oceanic and Atmospheric Administration (NOAA) recently measured that the global average of carbon dioxide(CO<sub>2</sub>), an important GHG in the atmosphere at 400 ppm(Dlugokencky and Tans, 2015). The impact of this accelerated change on a global scale is already being felt with increasing frequency of extreme events such as floods and droughts, rise in sea levels due to melting of polar ice caps which unchecked would result in the displacement of millions, acidification of water bodies endangering marine eco-system (Pachauri and Reisinger, 2007). AGW is majorly attributed to the emissions arising from human energy use (Karl and Trenberth, 2003) which

at present and for the foreseeable future revolves around combustion of fossil fuels (World Energy Scenarios, 2013). The combustion of fossil fuels has 9 ppm of CO<sub>2</sub> into the atmosphere in the years 2011-2012 alone(http://www.esrl.noaa.gov/gmd/ccgg/trends/ff.html) European Union (EU), a forerunner is adopting ambitious targets in mitigating climate change has set itself a goal of reducing of (GHG) emissions by 80% compared to 1990 by the year 2050. It has laid a clear route map for achieving the same with a huge stress on improving efficiency of energy systems and greater use of renewable energy.

Transportation is one area where fossil fuels are projected to remain highly dominant since most proposed alternatives (hydrogen, electricity, natural gas) have very low volumetric energy content (Züttel et al., 2010). In 2012, transportation accounted for nearly quarter of the GHG emissions in EU and whilst other sources have shown a gradual decline in GHG emissions between the years 1990 and 2007, the opposite has been true for the transport sector(Camarsa et al., 2015).

The passenger vehicle fleet is set to be double that of 2012 by the year 2035 even while the energy requirement

<sup>\*</sup> Corresponding Author: vijaishankar.bhavanishankar@kaust.edu.sa

is projected to remain to the same due to increase in efficiencies(Kalghatgi, 2014). Spark Ignition (S.I) engines fuelled by motor gasoline is projected to remain as the dominant propulsion power unit in light-duty vehicles (LDV)(EIA, Annual Energy Outook 2014). The thermal efficiency of these engines is limited by knock, a phenomenon that occurs due to auto-ignition in the unburnt gases before the flame front that originated at the spark reaches it. The use of fuels with superior octane quality is low hanging fruit that has been be exploited to increase the thermal efficiencies of these engines.



Figure 1. Increasing Carbon Dioxide Concentration in the Atmosphere (Dlugokencky and Tans, 2015)

Properties	Toluene	Ethanol	2- PE
Molecular Formula	C7H8	C <sub>2</sub> H <sub>6</sub> O	C <sub>8</sub> H <sub>10</sub> O
Molar Mass (Kg/mol)	0.092	0.046	0.122
RON	120	108	NA
S	17	9	NA
Density [kg/l]	0.866	0.784	1.017
<b>B.P</b> ( <b>K</b> )	373	371	493
LHV (MJ/kg)	40.6	26.7	36.7
ΔH <sup>°</sup> vap (KJ/mol)	37.3	42.3	69

Benzene, Toluene and Xylene (BTX) are presently added to base gasoline cut as much as 35 % to enhance its anti-knock quality. BTX, however are highly toxic and benzene is known carcinogen (NTP, 2014) which makes their reduction or removal from gasoline desirable. Bio-Ethanol is added to gasoline by mandate in USA, Brazil and Europe for its supposed environmental benefits also raises the fuel's octane rating. The claim of its environmental benefits has come under fierce criticism since first generation corn sugar ethanol provides dismal energy returns(Pimentel and Patzek, 2005)(Biofuels For Transportation, 2006)(Michel, 2012)(Charles et al., 2013). Ethanol addition also reduces the volumetric heat value of the fuel which increases specific fuel consumption.

2-Phenylethanol's molecular structure suggests that it possess a high resistance to auto-ignition. It has a high heat of vaporization which indicates to an enhanced charge cooling capability. Both these characteristics points towards its high octane quality. It is also food-grade substance implying zero toxicity with a volumetric lower heating value close of that of gasoline. Thus, 2-PE is a potential octane booster.

### 2. Octane Quality of 2-Phenylethanol

Three fuel's, neat FACE G (Fuels for Advanced Combustion Engines) gasoline (RON 96.8), FACE G + 20% 2-PE (v.v%) and FACE G + 20% Ethanol (v.v), knock response to spark time advance was studied in a single cylinder modified Cooperative Fuels Research (CFR) engine at one operating point presented in table 2.

### Table 2. Engine Operating Conditions

Engine	Operating		
Parameters	Conditions		
Cylinder Volume	$\approx 600 \text{ cm}^3$		
Engine Speed	600 rpm		
Equivalence Ratio	1		
Intake Air Temperature	<b>150</b> °C		
Intake Air Pressure	98 KPa		
Compression Ratio	6.5		
<b>Fuel Delivery</b>	Port Fuelled Injector		

2-PE's effect on FACE G's octane quality is similar to that of ethanol at this operating condition. The octane quality of such blends scales linearly on molar basis (Foong et al., 2014). The mole fraction of ethanol in these mixture is higher than that of 2-PE. Therefore, it is reasonable to conclude at this operating condition 2-PE has a greater octane quality.

The authors do recognize that neither the engine nor the operating condition is representative of modern gasoline engines. The performance and emission characteristics of 2-PE will be investigated further in engines across different operating conditions.



Figure 2. Knock Intensity with Advancing Spark Timing

# 3. Kinetic Modelling

2-PE sub-mechanism in the high temperature chemical kinetic model was developed adopting the reaction classes in the butanol mechanism by Sarathy et al. (Sarathy et al., 2012). The reaction classes as follows

- 1. Unimolecular Decomposition
- 2. H-atom Abstraction from fuel
- 3. Fuel Radical Decomposition
- 4. Fuel Radical Isomerization
- 5. Unimolecular Decomposition of Enol
- 6. H-atom abstraction from Enols
- 7. Keto-Enol Tautomerisation
- 8. Molecular Oxygen and Atomic Hydrogen addition to Enol
- 9. Decomposition of Enol Radicals

The sub-mechanism consists of 152 reactions involving 58 species. The rates of these reactions will be taken at high pressure limit and hence do not have any pressure dependence. The validation targets to be simulated are at 10 and 20 bar where these rates would hold good. The reactions and rates involving species formed in the reactions specified in the sub-mechanism were covered in the n-butyl benzene model by Diévart and Dagaut (Diévart and Dagaut, 2011). The chemistry of C0-C4 species were incorporated through the integration of ARAMCO MECH 1.4(Burke et al., 2014).

# 4. Results

The ignition delay times (IDT) of 2-PE/oxygen mixtures in argon were measured in a High Pressure Shock Tube (HSPT) for two pressure ranges, 8-11 bar and 18-23 bar. The measurements were done for two equivalence ratios, 0.5 and 1 at constant dilution of 95%, from 1075 K to 1520K. The IDT normalized to 10 bar (8-11 bar) and 20 bar (18-23 bar) are presented in Fig 3 and 4. There is negligible pressure dependence validating our choice to use high pressure limit rates in the model. The kinetic model could not be tested and validated at the time of writing this extended abstract as the rate rules for some reactions are yet to be added to the mechanism.



Figure 3. Ignition Delay Times at Phi 0.5



Figure 4. Ignition Delay Times at Phi 1

The experimental data was however compared to simulations of ethanol auto-ignition in a constant volume batch reactor using the gasoline surrogate mechanism from Lawrence Livermore National Laboratory(Mehl et al., 2011). The auto-ignition behavior of these fuels is indicative of their octane quality at different engine operating conditions. The similarity in IDT was expected since they had similar effect on FACE G's knock response as seen earlier. Ethanol is less reactive than 2-PE at relatively lower temperatures but its resistance to autoignition decreases with increase in temperature. This suggests that 2-PE might have a slightly lower RON and a greater MON than ethanol. Therefore its Octane Index (OI) might be lower in modern gasoline engines(Kalghatgi, 2001).

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# KINETIC MODELING OF CARBON BLACK FORMATION

Simple Kumar<sup>a</sup>, Preeti Aghalayam and Manoj T. Kandakure<sup>b</sup> <sup>a</sup>Indian Institute of Technology Madras, TN, Chennai – 600036, India <sup>b</sup>Aditya Birla Science and Technology Company Private Limited, Raigad - 410208, India

### Abstract

Carbon Black is an industrially manufactured form of elemental carbon used in the tire production, printer inks, industrial coatings and so on. Carbon Black is typically manufactured by Furnace Black process. Studies have shown that there are four major steps involved in solid particle synthesis namely precursor formation, nucleation, surface growth and coagulation & agglomeration. To model CB formation, a surrogate fuel is chosen as a simple representative of the Carbon Black Feedstock. In this case, Chrysene and Hexadecane are taken as representatives of aromatic and aliphatic components respectively. A detailed reaction mechanism for the combustion reactions of Chrysene and Hexadecane, leading to various gas-phase precursors of CB has been put together from various literature sources. This mechanism consists of 310 species and 2507 reactions. Incorporating such a kinetic mechanism in numerical simulations is computationally expensive. In this work, new reduced mechanisms containing fewer species and reactions are generated using an automated mathematically optimal mechanism reduction tool provided in the commercial kinetic software DARS. While these reactions are able to demonstrate well the first step in CB formation (i.e. the formation of gas-phase pre-cursors of CB via a complex network of reactions), further steps including the nucleation, surface growth, coagulation and finally the solid particle formation, are necessary. The simulations corresponding to these physical phenomena are performed in CHEMKIN PRO® software. Results are presented for the various simulations performed to produce solid CB by varying inlet and reactor parameters.

# Keywords

Carbon Black, detailed kinetic modeling, mechanism reduction, poly aromatic hydrocarbons, precursors, etc.

# Introduction

Carbon Black is elemental carbon in the form of near spherical particles of colloidal size, coalesced into particle aggregates and agglomerates, and are produced from partial oxidation or thermal decomposition of hydrocarbons.

Carbon Black is manufactured by the Furnace Black Process, which involves incomplete combustion of heavy aromatic oils known as Carbon Black Feed Stock (CBFS). The CBFS is typically a combination of coal tar oil and residual oils from crude distillation and catalytic cracking which contain heavy alkane and aromatic species.

Carbon Black formation includes several complex chemical and physical processes. As per the general understanding, solid Carbon Black Formation involves four major steps. First, the feedstock reacts to give gaseous precursors. These are Acetylenes, Benzenes and several Poly Aromatic Hydrocarbons (PAHs). These precursors then go a phase transformation producing first nascent solid particles called nuclei. This step is termed as the Nucleation step. Further these nascent particles grow by reacting with the gaseous precursors and then finally they grow in size by coagulating and agglomerating [1]. • Preeti Aghalayam, preeti@iitm.ac.in

# **Choice of Surrogate**

The CBFS is a complex mixture of several aromatic and aliphatic hydrocarbon species, with the exact composition depending on the source of the CBFS. For the purpose of reactor scale simulations, it is important to propose a "surrogate fuel". A surrogate fuel is a mixture of one or more fuels which have similar physical properties as that of the principle fuel and is able to mimic the chemical properties (combustion properties) of the more complex principle fuel.

The surrogate fuel for CBFS contains large aromatic and aliphatic hydrocarbons. Hexadecane and Chrysene are chosen to be representatives of aliphatic and aromatic hydrocarbon present in the feedstock.

# Development of suitable detailed gas phase kinetic mechanism

Detailed kinetic mechanisms for the combustion of hydrocarbons consist of thousands of species and several thousands of reversible reactions. Ergut et al. [2] have presented a detailed reaction mechanism for the combustion of aromatic components while investigating the formation of PAH from Ethyl Benzene and Ethyl alcohol flames. This reaction mechanism can predict the formation of CB precursors, including Acetylene and Benzene, and very large Poly Aromatic Hydrocarbons (referred to by the lumped name BINS) [3]. However, this mechanism does not include any large aliphatic hydrocarbons. Therefore, a skeletal reaction mechanism developed by Chang et al. [4] for the breakdown of large aliphatic hydrocarbons into smaller components is also used. This reaction mechanism is combined with the aromatic one, to generate a new reaction mechanism which consists of 310 species and 2507 reactions. This mechanism is termed as the "basecase" mechanism for further analysis [3].

The largest species considered in this reaction mechanism are labelled "BINs". They represent a 'lumped' species possessing molecular weights and number of carbons in a specified range. Table 1 depicts the various "BINs" used in our reactor simulations.

Species	Description	
BIN 1	a class of large PAHs up to $C_{24}H_{12}$ with	
	molecular mass of 201–400 amu	
BIN 2	a class of large PAHs up to C <sub>48</sub> H <sub>24</sub> with	
	molecular mass of 401–800 amu	
BIN 3	a class of large PAHs up to C <sub>96</sub> H <sub>48</sub> with	
	molecular mass of 801–1600 amu	

Table 1: BINs present in the basecase mechanism

### **Mechanism Reduction**

In the recent past, computational fluid dynamic codes have undergone tremendous advances and are capable of incorporating chemical kinetic mechanisms to model reactive systems. While detailed reaction mechanisms for combustion are of critical importance, they present the major drawback of being very expensive, computationally. Thus, there is the need for mathematically reduced, optimal, reaction mechanisms, which, while retaining the fundamental structure of the full mechanism, are not as large and expensive, and can thus yield results quickly and reliably.

Here we have generated a reduced mechanism using the mechanism reduction module provided by commercial software DARS which uses Necessity Analysis to allot necessity coefficients for various species present in the mechanism.

At first, using the basecase mechanism, Perfectly Stirred Reactor (PSR) simulation is performed at 2000K and 1atm, for a residence time of 0.01 seconds. The inlet feed consists of (0.47 mass fraction) Chrysene and (0.47 mass fraction) Hexadecane as fuel and (0.06 mass fraction) Oxygen as the oxidizer. While providing the operating parameters and solver settings, DARS also allows us to specify the necessary species for mechanism reduction. In this case, the reactants are chosen as the necessary species as we want them to be present in our subsequent reduced mechanism

disregarding their necessity coefficients. This simulation provides us with necessity coefficients for all the species, which are then used for mechanism reduction. The basic idea of this reduction is to generate a reduced mechanism, having the lowest number of species, without losing any significant amount of accuracy in comparison to the basecase mechanism. The process of achieving this reduction is iterative. A general number of species close to 30% reduction is taken and the subsequent PSR simulations over the temperature range of 1500K to 2500K (usual operating temperature for CB production) are performed. Then the exit mass fractions for some of the species are plotted against the inlet temperature and were compared with the results of basecase mechanism. After several iterations, RM-2000 K, consisting of 210 species and 1947 reactions, was found to produce the best match for almost all the plots (see Table 2). Going any further down meant significant compromise in the accuracy of the predicted results.

Table 2: Basecase and Reduced Mechanisms

	Base Case	RM- 2000 K	% reduction
Species	310	210	32
Reactions	2507	1947	22

The mass fractions of various reactants and products are plotted in figures 1 - 3.



Figure 1: Exit Mass Fractions of the reactants

Starting from 1500K, the reduced mechanism follows the trendline set by the original basecase mechanism. This pattern is observed in all the mass-fraction plots of reactants and products. The comparison plots show that the reduced mechanism is able to mimic the results produced by the basecase mechanism and we can use this mechanism further to perform simulations for Carbon Black formation.

The reaction mechanism presented thus far consists entirely of gas-phase species. Therefore, the usefulness of these mechanisms (whether detailed or reduced), is only up to the formation of gas-phase precursors of Carbon Black.



Figure 2: Exit Mass Fraction of Products



Figure 3: Exit Mass Fraction of Products

### Surface Kinetic Mechanism

The gas phase reactions give rise to the gaseous precursors, which then further lead to the formation of solid particles. Now to account for all the reactions leading on to the formation and size increment of solid particles, a mechanism needs to be developed to define the physic-chemical phenomenon taking place in simple reaction steps with rates expressed in Arrhenius form. The formation of solid particles from the gaseous species is a complex process. Frencklach and coworkers [5] proposed that the first solid carbon particles are created by the dimerization of two Pyrene molecules. This reaction is represented as the nucleation step and is included in the chemistry set.

 $2C_{16}H_{10} \Rightarrow 32C(B) + 20H(se) + 28.72$ open(se) Here, two pyrene molecules combine together to give a bulk carbon particle with thirty two carbon atoms and twenty hydrogen atoms attached on the surface with 28.72 open surface sites.

After the nuclei are formed, they start to interact with each other as well as with the gas mixture around them. While particle-particle interactions such as coagulation are non-chemical processes, interactions between particles and the surrounding gas mixture can result in chemical processes taking place on the particle surface. To include the effects from all these surface processes, a surface mechanism is needed to describe all surface reactions and associated surface species on the particle. The Particle Tracking feature provided by CHEMKIN PRO<sup>®</sup>, then determines the impact of individual surface reactions on the particle sizes from the expression of the surface reactions.

The Surface Kinetic Mechanism derived here includes all these steps. The particle inception is modeled as Nucleation Reaction and this mechanism also consists of Surface Growth reactions, Poly Aromatic Hydrocarbons (PAH) condensation and Oxidation reactions. Surface growth is represented by Hydrogen Abstraction  $C_2H_2$  Addition (HACA) steps proposed by Frenklach et al [5].

Marr [6] proposed that PAH condensation on the particle surface also contributes significantly to the particle mass growth. Several PAHs contribute in this step including the high molecular weight species BINS. A simple condensation reaction can be represented as:

 $aPAH + bH(se) => cC(B) + dopen(se) + eH_2$ where a, b, c, d and e are stoichiometric coefficients.

Neoh et al [7] proposed that in this setup, oxidation of bulk carbon by hydroxyl molecule is the dominant one and this was the only oxidation step included in the mechanism.

# **Particle Tracking**

CHEMKIN PRO<sup>®</sup> uses two different methods for Particle Tracking: Method of Moments and Sectional Method. In the present work, method of moments has been employed to perform the simulations. Without making any assumptions about the form of the particlesize distribution function, the method of moments can provide overall properties of a particle system such as number density, total particle volume fraction, total particle surface area density, and average particle size.

### **Results and Discussions**

A PSR-PFR (Plug Flow Reactor) system in CHEMKIN PRO<sup>®</sup> is used to allow the gaseous reactions to take place in homogeneous conditions and lead to the formation of solid particles.

Inlet: The inlet feed contains 0.65 mole fraction of Nitrogen, 0.2 mole fraction of Chrysene, 0.05 mole fraction of Hexadecane and 0.1 mole fraction of Oxygen flowing in at the rate of 7.5 kg/sec. The inlet feed temperature is varied from 1100K to 2000K.

PSR: The PSR pressure is kept at 1 atm and the residence time is set at 0.02 seconds.

PFR: The PFR length is chosen to be 5 m and the reactor is modeled assuming adiabatic conditions. The PFR diameter is varied from 0.1 m to 0.5 m.

Figure 4 shows the plot of average particle class (number of bulk species molecules in a particle core) against the inlet feed temperature. There's an apparent increase with the rise in temperature and the PFR diameter as well. The average particle diameter also increases with the increase in inlet feed temperature (see Figure 5) while the particle number density shows a non-monotonic behavior (see Figure 6). Therefore with the increase in temperature, coagulation and agglomeration become dominating and maybe the surface growth also gets a boost with the temperature increase. Lockwood et al. [8] and Naydenova [9] have also reported the increasing trend in average particle size with increase in inlet gas temperature for this studied range. However; Ono et al. [10] have reported that with increase in temperature, nucleation may dominate, leading to lower particle sizes and higher number density. This phenomenon is not entirely observed in our simulations at this point and will be investigated further.



Figure 4: Average Particle Class



Figure 5: Average Particle Diameter



### Figure 6: Particle Number Density

The predicted exit gas temperatures are greater than the inlet gas temperatures (see Figure 7) which support the exothermic nature of the reactions.



Figure 7: Exit Gas Temperature

#### **Summary and Conclusion**

The results have shown that the reduced mechanism is able to closely approximate the values predicted by the basecase mechanism as far as the gas phase species concentrations are concerned. The predictions reveal that the average particle size increases with increase in inlet gas temperature. Further investigation will be carried out to study this phenomenon in detail. The surface mechanism and the interactions of the gas phase and surface chemistries will be also examined closely for developing further understanding.

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# **Kinetics of Naphthalene Formation via HACA Pathways**

Alexander M. Mebel,<sup>1</sup> Zhaohui Wang,<sup>2</sup> Feng Zhang,<sup>2</sup> Ahren W. Jasper,<sup>3</sup> Nicole J. Labbe,<sup>4</sup> Raghu Sivaramakrishnan,<sup>4</sup> Lawrence B. Harding,<sup>4</sup> James A. Miller,<sup>4</sup> Stephen J. Klippenstein<sup>4,\*</sup>

<sup>1</sup>Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33199 <sup>2</sup>National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, P. R. China

<sup>3</sup>Combustion Research Facility, Sandia National Laboratories, Livermore, CA 94551 <sup>4</sup>Chemical Sciences & Engineering Division, Argonne National Laboratory, Argonne, IL 60439

# Keywords

# HACA, Naphthalene, Ab Initio Transition State Theory, Master Equation, Combustion Kinetics

The hydrogen abstraction acetylene addition (HACA) mechanism is commonly considered to provide an important route to ring expansion in polycyclic aromatic hydrocarbons. The theoretical study of Ref. 1 provides a wide-ranging exploration of the energetics for a variety of HACA related pathways of possible relevance to the ring expansion from benzene to naphthalene. In this work, we explore the kinetic role of these pathways in the formation of napthalene within a variety of flame environments. First, the ab initio transition state theory based master equation (AITSTME) approach is used to predict the temperature and pressure dependence of the relevant rate processes. The predicted rate coefficients are then incorporated in global chemical models for the combustion of a few protopytical fuels such as acetylene, ethylene, ethane, and toluene.

The present AITSTME calculations build upon the earlier ab initio study of Ref. 1 with improved treatments for various aspects including variational treatments of the key low barrier processes, variable reaction coordinate transition state theory treatments for a few barrierless processes, explorations of the appropriateness of CASPT2 versus CCSD(T) evaluations, and explicit consideration of hindered rotors. For the  $C_6H_5 + C_2H_2$  and  $C_6H_5 + C_2H_4$  reactions the potential energy surface is reexplored with B2PLYPD3/aug-cc-pVDZ rovibrational analysis and estimates of the CCSD(T)/CBS energies at these B2PLYPD3 geometries. These analyses build upon the earlier studies of Refs. 2 and 3. The requisite energy transfer parameters are explicitly evaluated from trajectory simulations. The master equation analysis provides modified Arrhenius expressions in PLOG format and includes proper treatment of well merging phenomena. Reaction path flux analyses are used to explore the role of the various HACA pathways in representative flames. The role of equilibrium reversals for various weakly bound intermediates is also explored. Preliminary results suggest an increased role for naphthyne arising from direct H loss of naphthyl radicals. The results also indicate that under typical flame conditions, naphthalene is the predominant product of acetylene addition to the C<sub>8</sub>H<sub>7</sub> radicals formed by H abstraction from styrene in the ortho position in the ring or in the side-chain CH<sub>2</sub> group.

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# EXPERIMENTAL KINETIC STUDY OF SEVERAL REACTIONS CRITICAL TO PAH FORMATION: VINYL + 1,3-BUTADIENE, VINYL + ACETYLENE AND PHENYL + ACETYLENE

Z. J. Buras, <sup>†, \*</sup> G. Liu, <sup>†, ‡</sup> Z. Gou, <sup>†, ‡</sup> E. E. Dames, <sup>†</sup> S. S. Merchant, <sup>†</sup> R. M. I Elsamra, <sup>†, §</sup> W. H. Green<sup>†</sup>

<sup>†</sup>Massachusetts Institute of Technology, Department of Chemical Engineering Cambridge, MA 02139

<sup>‡</sup>Tianjin University, School of Chemical Engineering & Technology Tianjin, China 300072

> <sup>§</sup>Alexandria University, Department of Chemistry, Alexandria, Egypt 21321

# Abstract

Using laser flash photolysis coupled with visible laser absorbance and photoionization time-of-flight mass spectrometry (PI TOF-MS) we have experimentally studied several reactions of importance to PAH formation. Specifically, overall rate coefficients and quantitative product branching fractions have been measured for vinyl + 1,3-butadiene, vinyl + acetylene and phenyl + acetylene. All of these reactions share a commonality in that their product distributions are dominated by a radical adduct channel and a chemically-activated H-loss channel. The competition between the two product channels is highly temperature and pressure-dependent, as many theoretical studies have predicted. In all three cases we provide the first relatively low temperature (<700 K) quantification of the branching fractions. Our experimental findings are compared to theoretical predictions so that they can be accurately extrapolated to combustion relevant conditions.

# Keywords

Soot, experimental kinetics, flash photolysis, laser absorbance, mass spectrometry

### Introduction

Formation of the first aromatic ring in combustion systems is a critical step in the pathway from small unsaturated hydrocarbons to polycyclic aromatic hydrocarbons (PAH) and eventually to soot (Richter and Howard, 2000). Besides the well-studied propargyl radical recombination, two other routes to benzene that have received attention over the last thirty years are vinyl radical + 1,3-butadiene ( $C_2H_3$  + 1,3- $C_4H_6$ ) (Westmoreland et al., 1989; Xu et al., 2011), and the sequence vinyl + acetylene  $(C_2H_3 + C_2H_2) \rightarrow n$ - $C_4H_5$  (Miller et al., 2000) followed by  $n-C_4H_5 + C_2H_2$ (Senosiain and Miller, 2007). In the former case there are no direct experimental measurements of either the overall rate coefficient or the product branching against which to compare the theoretical predictions. For the initial step of the latter case  $(C_2H_3 + C_2H_2)$ , there are experimental measurements of the overall rate coefficient over a wide temperature range (Knyazev et al., 1996), and of the product branching at relatively high (>1000 K) (Fahr and Stein, 1989) and low (≤400 K) (Callear and Smith, 1986) temperatures where only one product dominates. However, there are no measurements of the branching in the intermediate temperature range where the pressure-dependence is predicted to play a large role (Miller, et al., 2000).

Once benzene is formed it can enter the hydrogen abstraction acetylene addition (HACA) mechanism to eventually form PAH. One of the first steps in this mechanism is phenyl radical ( $C_6H_5$ ) +  $C_2H_2$ . This reaction has been studied extensively both experimentally and theoretically because of its central importance to PAH formation (Richter et al., 2000; Tokmakov and Lin, 2003). To our knowledge, however, there is still no measurement of the product branching that can be used to validate the predicted T,P-dependence.

Using laser flash photolysis coupled with visible laser absorbance and photoionization time-of-flight mass spectrometry (PI TOF-MS) we have provided critical experimental measurements of overall rate coefficients and product branching for the reactions mentioned above. In all three cases ( $C_2H_3 + 1,3-C_4H_6$ ,  $C_2H_3 + C_2H_2$  and  $C_6H_5 + C_2H_2$ ) our results enable us to recommend which theoretical predictions are most accurate and should therefore be used in future combustion models.

<sup>•</sup> To whom all correspondence should be addressed

# Experimental

Our experimental apparatus has the capability to make time-resolved measurements of radical chemistry using two techniques simultaneously: laser absorbance and PI TOF-MS. Both techniques rely on 266 nm laser photolysis of a suitable chemical precursor (C<sub>2</sub>H<sub>3</sub>I or C<sub>6</sub>H<sub>5</sub>I) to generate the initial radical of interest (C<sub>2</sub>H<sub>3</sub> or C<sub>6</sub>H<sub>5</sub>) in addition to I atom. Radicals are generated in a heated, stainless steel, continuous flow reactor designed to accommodate a wide range of operating conditions (300-700 K and 4-100 Torr). The stable co-reactant (either  $1,3-C_4H_6$  or C<sub>2</sub>H<sub>2</sub>) was present in great excess (3-4 orders of magnitude above the radical concentration) to ensure pseudo-first-order conditions. Helium was used as a bath gas. All experiments were conducted such that the gas in the reactor was replenished between each photolysis shot.

The laser absorbance portion of the apparatus has been described in detail elsewhere (Ismail et al., 2007). Briefly, a Herriott multiple-pass alignment of the quasi-continuous probe laser is employed to obtain path lengths up to 40 m. The probe laser has a tunable output wavelength that covers most of the visible spectrum. Concentration profiles of C<sub>2</sub>H<sub>3</sub> and C<sub>6</sub>H<sub>5</sub> were measured using their relatively strong absorbance features at 423.2 and 434 nm, respectively. Overall rate coefficients can then be obtained by fitting the measured decays to a kinetic model. The initial concentration of I atom, [I]<sub>0</sub>, was also measured using a separate diode laser tuned to its  $F = 3 {}^{2}P_{1/2} \leftarrow F = 4 {}^{2}P_{3/2}$  hyperfine atomic transition. We assumed [I]<sub>0</sub> = [R]<sub>0</sub> in our subsequent kinetic models, where R = C<sub>2</sub>H<sub>3</sub> or C<sub>6</sub>H<sub>5</sub>.

The PI TOF-MS portion has also been described recently (Middaugh, 2014). Briefly, a small portion of the gas in the reactor is sampled through a small pinhole in the center of the reactor, collimated into a molecular beam by a skimmer and then ionized using pulsed 118 nm (10.5 eV) radiation. The 118 nm radiation is generated by frequency tripling the 355 output of an Nd:YAG laser in a mixture of xenon and argon. The cations formed are then steered by a set of ion optics to the detector of the TOF-MS. The delay between the photolysis and photoionization lasers can be stepped with nanosecond resolution, enabling time-resolved measurements of the full mass spectrum. In this manner, the growth of different product branches can be measured and quantified.

# **Results and Discussion**

To facilitate the discussion about each of the three individual reactions, it is helpful to first note their similarities. *Figure 1* shows schematically the kinetic models adopted to describe each system. The most important parallels are the following: 1. Each model includes a unimolecular decay term,  $k_{uni}$ , that capture many indiscernible first order loss processes such as

diffusion out of the sampling region, decomposition and reaction with the wall or precursor molecule.  $k_{uni}$  is quantified by fitting the absorbance decay of R without any excess reagent. 2. Each model also includes a selfreaction term, k<sub>self</sub>, that is known from literature (Ismail et al., 2009; Tranter et al., 2010). 3. For the reaction of interest, we expected and observed only two major channels: collisional stabilization to a radical adduct and chemically activated loss of hydrogen. For all three systems, we quantified the product branching to the Hloss channel,  $\alpha$ , using PI TOF-MS. This channel was amenable to quantification because a stable species is produced (cyclohexadiene isomers, vinylacetylene and phenylacetylene) that has a known PI cross section, whereas the same quantity for the radical adduct is usually unknown or highly uncertain.



Figure 1: Simplified schemes used to model the three systems studied here: A. Vinyl + 1,3-Butadiene, B. Vinyl + Acetylene and C. Phenyl + Acetylene. Asterisks denote ro-vibrationally excited isomers.

Important differences between the three systems are discussed in the following subsections.

# Vinyl + 1,3-Butadiene

By probing the visible absorbance of  $C_2H_3$  at different excess  $1,3-C_4H_6$  concentrations, we have provide the first direct experimental measurement of

the overall rate coefficient,  $k_{C2H3+1,3-C4H6}$  (*Figure 2*) (Buras et al., 2015). Clearly, previous predictions were inaccurate, so we provided our own predictions that match the experiments well and can be extrapolated to a wide range of combustion relevant conditions (300-2000 K and 1 Torr He to high-P limit).

We also measured  $\alpha_{c-C6H8}$  and found it to be <20% even up to 700 K in 4 Torr He (*Figure 3*). The remaining majority of the product distribution is expected to be the linear resonantly-stabilized radical adduct shown in *Figure 1A*. Our theoretical results over-predict the total branching to C<sub>6</sub>H<sub>8</sub> (consisting almost entirely of cyclohexadiene) by a factor of five. We attribute this discrepancy mostly to uncertainty in the collisional energy transfer model used in the theoretical predictions. At combustion relevant conditions of high-P and larger bath gas molecules (i.e., N<sub>2</sub> and O<sub>2</sub>), this uncertainty is less important.



Figure 2: Arrhenius plot of our measured values of  $k_{C2H3+1,3-C4H6}$  and comparison with literature. Reprinted with permission from Buras et al. (2015). Copyright 2015 American Chemical Society.



Figure 3: Comparison between measured branching fraction of  $C_2H_3 + 1,3-C_4H_6$  to  $c-C_6H_8$  (cyclohexadiene isomers) and sum of predicted branching fractions to all  $C_6H_8$  isomers (mostly consisting of cyclohexadiene). Reprinted with permission from Buras et al. (2015). Copyright 2015 American Chemical Society.

# Vinyl + Acetylene

Despite the chemical simplicity of the two reactants, this reaction system actually required the most complex model, as shown in Figure 1B. The fundamental issue is that H generated from chemically activated H-loss can add to the triple bond of acetylene to regenerate more vinyl radical, necessitating the inclusion of H in the model. The other two reaction systems studied here also generate H, but in those cases it is not necessary to include H in the model because it will not affect either the overall rate coefficient or  $\alpha$ . Fortunately, two of the bimolecular reactions involving H have been measured previously in the literature (H +  $C_2H_2 \, (Baulch \mbox{ et al., } 1992) \mbox{ and } H + C_2H_3 \mbox{ (Monks \mbox{ et al., } }$ 1995)). The rate coefficients for the two remaining H consuming channels,  $k_{n-C4H5-isom}$  and  $k_{H-uni}$ , were treated as additional fit parameters in the model.

Because of the complexity of this system, it was not possible to abstract values of  $k_{C2H3+C2H2}$  from the absorbance decay of C<sub>2</sub>H<sub>3</sub> alone. Instead,  $k_{C2H3+C2H2}$ and  $\alpha_{C4H4}$  were fit to the growth and decay of C<sub>4</sub>H<sub>4</sub> and C<sub>4</sub>H<sub>5</sub> observed using PI TOF-MS (*Figure 4* and *Figure 5*). This is in contrast to the other two systems where values of  $\alpha$  could be obtained simply by measuring the "steady-state" concentration of the stable H-loss product (i.e., it was not necessary to fit the growth observed in the TOF-MS). Despite these complicating factors, our measured values of  $k_{C2H3+C2H2}$  and  $\alpha_{C4H4}$  are in excellent agreement with the predictions of Miller et al. (2000). The  $\alpha_{C4H4}$  result is particularly noteworthy, as it represents the first experimental validation in this interesting T,P-dependent range.



Figure 4: Arrhenius plot of our measured values of  $k_{C2H3+C2H2}$  and comparison with literature.

### Phenyl + Acetylene

Unlike the previous two systems, we did not attempt to measure the overall addition rate coefficient  $k_{C6H5+C2H2}$  because it has already been measured extensively. Instead, we focused only on  $\alpha_{C6H5C2H}$  and observed excellent agreement with the predictions of (Richter, et al., 2000) (*Figure 6*) and poor agreement with (Tokmakov and Lin, 2003) (not shown). We are

currently investigating the source of the discrepancy between the two literature predictions.



Figure 5: Comparison between our measured branching fraction of  $C_2H_3 + C_2H_2$  to  $C_4H_4$  (vinylacetylene) and literature predictions.



Figure 6: Comparison between our measured branching fraction of  $C_6H_5 + C_2H_2$  to  $C_6H_6C_2H$  (phenylacetylene) and literature predictions.

### Conclusions

Based on our experimental measurements of three reactions important to soot formation, we recommend using the following theoretical predictions in future combustion models: 1. Our predictions for  $C_2H_3 + 1,3-C_4H_6$ , 2. Miller et al. for  $C_2H_3 + C_2H_2$ , and 3. Richter et al. for  $C_6H_5 + C_2H_2$ .

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# A NEW PATHWAY TO FORM NAPHTHALENE FROM THE ADDITION OF FULVENALLENYL AND PROPARGYL RADICALS: A QUANTUM CHEMISTRY/MASTER EQUATION STUDY

Edward Ross,<sup>\*</sup> Gabriel da Silva Department of Chemical and Biomolecular Engineering The University of Melbourne, Victoria 3010, Australia

### Abstract

This work examines the reaction mechanism and kinetics of the recombination reaction between the fulvenallenyl radical and the propargyl radical. Quantum chemistry calculations were first used to find several pathways to forming naphthalene via fulvalene and azulene. It was found that the fulvalene pathway was the most energetically favourable, with a maximum barrier that is 28 kcal/mol below the initial entrance channel. On the other hand, the more complex azulene pathway was found to have a maximum barrier that is 16 kcal/mol below the entrance channel. RRKM/master equation calculations were subsequently performed to determine the kinetics for this chemically activated process. The azulene pathway was found to contribute a very minor amount to the formation of naphthalene, hence a model only consisting of the fulvalene pathway was sufficient to determine the kinetics. At lower temperatures, quenching of the initial adduct was found to compete with dissociation back to the original reactants. Rate coefficient expressions for the chemically activated formation of naphthalene, naphthyl radicals was found to compete with dissociation back to the original reactants. Rate coefficient expressions for the chemically activated formation of naphthalene, naphthyl radicals and fulvalene were then obtained, for inclusion in relevant kinetic models.

# Keywords

Ab initio, PAH, Pyrolysis

# Introduction

The fulvenallenyl radical  $(C_7H_5)$  is a resonance stabilised radical (RSR) which is formed in appreciable quantities during the combustion and pyrolysis of toluene. It has been detected in prior toluene pyrolysis experiments (Zhang et al., 2009; Yuan et al., 2015) and its formation primarily occurs via H-loss from fulvenallene (da Silva et al., 2011: Giegerich and Fischer, 2013). Its thermal decomposition chemistry has also been investigated (da Silva et al., 2011), whereby it was concluded that the formation of diacetylene and the propargyl radical  $(C_4H_2 + C_3H_3)$  were the dominant decomposition products, while the formation of  $C_5H_3 + C_2H_2$  was deemed to be a minor channel.

The fulvenallenyl radical shares structural similarities with other RSRs that are present in flames such as the propargyl and cyclopentadienyl radicals. Hence, it has been suggested that the fulvenallenyl radical should undergo bimolecular growth reactions with other RSRs to form polycyclic aromatic hydrocarbons (PAHs), species which are long thought to be the immediate precursors of soot. While the formation and thermal decomposition chemistry of the fulvenallenyl radical is relatively well understood, there are only a limited number of studies which investigate and/or incorporate  $C_7H_5$  molecular weight

growth chemistry. Matsugi and Miyoshi (2012) conducted a theoretical investigation of the C9H7 energy surface, which included examining the kinetics of fulvenallenyl with acetylene  $(C_2H_2)$ . These authors found that at 1 atm the formation of the indenvl radical (C<sub>9</sub>H<sub>7</sub>) was the predominant product at temperatures up to 2000 K, while the subsequent dissociation to form propargyl plus o-benzyne (C<sub>6</sub>H<sub>4</sub>) became dominant at higher temperatures. In their modelling study on the pyrolysis of toluene, Matsugi and Miyoshi (2013) incorporated several bimolecular reactions involving the fulvenallenyl radical into their model. These authors estimated the kinetics for these reactions from analogous reactions involving the propargyl radical, and the results from their mass flux analysis indicated that these reactions have an important contribution to the formation of naphthalene and phenanthrene during the pyrolysis of toluene. Yuan et al. (2015) also incorporated these reactions into their toluene pyrolysis model with the kinetic data also estimated from analogous reactions. While both of these authors recognise the importance of the fulvenallenyl radical in the formation of PAH species, it is clear that more accurate expressions are required to better quantify the kinetics of these reactions.

This work examines the reaction between the fulvenallenyl radical and the propargyl radical in the

formation of naphthalene, using a combined quantum chemistry/master equation approach. Ab initio calculations are employed to determine the underlying reaction mechanism, which is then used as a basis for performing master equation simulations. Kinetic rate expressions were then obtained from these simulations.

### Methods

Electronic structure calculations were performed using the Gaussian 09 software. The G3X-K composite method was used to evaluate the energies of all the stationary point structures and transition states. RRKM/master equation simulations were performed using the Multiwell 2013 software suite.

### **Mechanism Description**

### Fulvalene Pathway

Presented in Figure 1 is the reaction mechanism for the fulvenallenyl-propargyl recombination reaction via the fulvalene pathway.



Figure 1. Energy surface for the  $C_7H_5 + C_3H_3$ reaction: the fulvalene pathway (energies in kcal/mol).

Omitted from Figure 1 are the other possible initial adducts that can form from the addition of these two radicals. These other adducts have energies that lie between 50-60 kcal/mol below the initial entrance channel, and while they are able to isomerise amongst one another with barrier heights of between 30-45 kcal/mol, only the initial adduct depicted in the figure (W1) can directly lead on to the other structures. Once formed, W1 can undergo ring formation to produce the bicyclic carbene species W2 after passing through the transition state TS1. This step corresponds to a barrier height of 33.1 kcal/mol and represents the largest energy barrier for this pathway. A simple 1,2 H-shift then results in the formation of fulvalene (W3). This process is exothermic by over 60 kcal/mol, owing to the stability of fulvalene. The rearrangement of fulvalene to naphthalene (W4) can be thought of as being analogous to the well-documented rearrangement of fulvene to benzene (Miller and Klippenstein, 2003; Madden et al. 1996), however unlike this reaction we found the fulvalene rearrangement to take place over a single transition state (**TS3**). Due to the concerted nature of this process, the barrier for this isomerisation is rather large (71.1 kcal/mol). Simple C-H bond cleavage follows the formation of naphthalene to form either 1-naphthyl or 2-naphthyl radicals, with an estimated BDE of 112 kcal/mol for both reactions, in accord with the value corresponding to H loss in benzene (Miller and Klippenstein, 2003).

### Azulene Pathway

Presented in Figure 2 is the mechanism for the azulene formation pathway. It should be noted that in order to save space, the mechanism displayed in the figure is a simplification of the actual reaction mechanism; over twenty reaction steps were found, spanning several parallel reaction paths. What is pictured corresponds to the minimum energy path for the azulene pathway. For steps which consist of multiple rearrangements, parallel lines are drawn below the transition state, with each energy corresponding to the largest barrier along each series of steps.



Figure 2. Energy surface for the  $C_7H_5 + C_3H_3$ reaction: the azulene pathway (energies in kcal/mol).

This mechanism proceeds from the initial adduct W5, which has an energy similar to that of W1. A series of 1,2 H-migrations around the ring results in the formation of the species W6. W6 can then undergo ring closure to form the bicyclic species W7, after surmounting the transition state TS6 which lies 37.6 kcal/mol below the entrance channel. Another series of steps, which include H-shifts and ring formations/expansions then results in the formation of azulene (W8). The highest barrier along this series of steps corresponds to the 1,3 H-shift from the CH2 group located on the five-membered ring, to the carbon on the six-membered ring. Finally, azulene can rearrange to naphthalene via a two-step process at an overall barrier of 74.8 kcal/mol. Our mechanism for this rearrangement was found to be virtually identical to the norcaradiene-vinylidene mechanism that was proposed by Becker et al. (1980).

### **RRKM/Master Equation Simulations**

### Mechanism and Model Simplification

The mechanism that has been described above consists of a large number of intermediate structures, multiple initial adducts and several parallel pathways. This gives rise to a complex phenomenological model which consists of a large number of species that are not currently included in kinetic models. Thus, a reduced phenomenological model which still captures the dynamic behaviour of the complete mechanism is desired, such that it can be feasibly implemented in kinetic models. As a result, initial simulations were performed on different components of the mechanism in order to determine whether a simpler model could be used to determine the kinetics for the fulvenallenyl + propargyl reaction.

Firstly, sets of simulations were performed on the full mechanism, with each of the different starting adducts designated as the chemically activated species in separate simulations. It was found that along the entire range of conditions examined, the total contribution of all the other initial adducts to the formation of key species (fulvalene, naphthalene, naphthyl radicals) was relatively minor. At 2000 K and 0.01 atm the total contribution of all the other adducts was around 2-3% while at 600 K, this value was at around 10 %. Although the other adducts contribute significantly to the overall  $C_7H_5 + C_3H_3$ recombination rate at lower temperatures, most of the species that form in these instances are other intermediate structures that do not undergo any further reaction. Therefore it is apparent that W1 is the only adduct which is significant to the subsequent formation of PAHs in this reaction. Furthermore, simulations were performed on the fulvalene mechanism only in order to assess the importance of the azulene mechanism. It was found that the yields of all the key species were almost identical to those obtained from the simulations that were performed on the full mechanism. Thus, it was determined that the azulene mechanism is of negligible importance to the kinetics of the fulvenallenyl + propargyl reaction, and that the much simpler fulvalene mechanism is sufficient to describe the kinetics of this reaction.

### Determination of Rate Coefficient Expressions

Presented in Figure 3 is a plot showing the kinetics of total product formation as a function of temperature at a variety of different pressures, as well as for the high pressure limit. The extent of falloff is similar to that determined by Georgievskii et al. (2007) for the propargyl + propargyl reaction and becomes significant at 2000 K across the entire range of pressures that were examined. It also appears that the collisionless limit has been reached at 2500 K for the 0.01 atm and 1 atm simulations, where the activated  $C_{10}H_8$  adducts completely dissociate to either the

reactants or to napthyl radicals + H. Consistent with other chemically activated reactions, trends were observed in the yield of each major species. At low temperatures (< 1000 K), the initially formed adduct (W1) is unreactive and gets collisionally stabilised upon formation. As the temperature is increased, fulvalene and naphthalene start to form, followed by the formation of both naphthyl radicals + H. However, back dissociation to reform the original radicals also becomes increasingly prominent at higher temperatures, resulting in the falloff effects discussed above.





Figure 3. Rate coefficient plot for  $C_7H_5 + C_3H_3 \rightarrow$ Products as a function of temperature.

A plot is presented below in Figure 4 for the chemically activated rate coefficient for the formation of naphthalene at 0.01 atm, which is in accord with the effects discussed above. The parabolic trend can be explained by the fact that negligible naphthalene is formed at lower temperatures due to collisional deactivation of the initial adduct being dominant. At intermediate temperatures (1000 - 1200 K), the net effects of collisional deactivation and falloff are at their minimum, and so the calculated formation rate peaks at these temperatures. When the temperature is further increased, falloff begins to dominate and so the calculated rate then decreases rapidly, although direct (well-skipping) production of napthyl radicals does contribute to PAH formation under these conditions.



Figure 4. Rate coefficient plot for  $C_7H_5 + C_3H_3 \rightarrow$ naphthalene as a function of temperature (at 0.01 atm).

Table 1. Modified Arrhenius expressions for key reactions in  $C_7H_5 + C_3H_3$ :  $k(T,p) = AT^n exp(-E_a/RT)$ . Pressure at 1 atm, units of  $E_a$  are in cal/mol.

Reaction	A	n	Ea
$C_7H_5 + C_3H_3 \rightarrow W1 (300-1000 \text{ K})$	6.12×10 <sup>-14</sup>	0.49	-770
$C_7H_5 + C_3H_3 \rightarrow W1 \ (1000-2000 \ K)$	$3.04 \times 10^{80}$	-26.8	53 500
$C_7H_5 + C_3H_3 \rightarrow \text{fulvalene} (300\text{-}1000 \text{ K})$	1.21×10 <sup>-34</sup>	6.72	-1 380
$C_7H_5 + C_3H_3 \rightarrow \text{fulvalene} (1000-2500 \text{ K})$	$3.19 \times 10^{127}$	-39.6	101 200
$C_7H_5 + C_3H_3 \rightarrow naphthalene (600-1000 \text{ K})$	1.11×10 <sup>-8</sup>	-1.20	20 100
$C_7H_5 + C_3H_3 \rightarrow naphthalene (1000-2500 \text{ K})$	$3.19 \times 10^{86}$	-27.8	87 400
$C_7H_5 + C_3H_3 \rightarrow C_{10}H_7 + H \ (1000-2500 \text{ K})$	$2.38 \times 10^{49}$	-16.9	73 600

Presented in Table 1 are rate coefficient expressions for each of the important chemically activated reactions, in modified Arrhenius form at a pressure of 1 atm. When determining an expression for  $C_7H_5 + C_3H_3 \rightarrow W1, C_7H_5 + C_3H_3 \rightarrow naphthalene and$  $C_7H_5 + C_3H_3 \rightarrow$  fulvalene, it was necessary to derive two separate modified Arrhenius expressions for low and high temperature regimes, in order to obtain a more accurate fit to the calculated rate coefficient data. These rate coefficients can be implemented in kinetic models where fulvenallenyl is expected to be present in significant concentrations, i.e. toluene pyrolysis. However before these are introduced into kinetic models, the unimolecular decomposition kinetics of each of the important  $C_{10}H_8$  intermediates (W1, fulvalene, naphthalene) also need to be determined. The C<sub>10</sub>H<sub>8</sub> master equation model presented here is currently being used to obtain these results.

### Conclusion

The kinetics for all of the major reactions corresponding to the recombination of propargyl and fulvenallenyl radicals was determined using a combined quantum chemistry/master equation approach. It was found that the fulvalene mechanism was the only pathway that was significant for determining the kinetics for this recombination process. The observed falloff behavior was found to be typical for a chemically activated reaction, while the trends in the rate coefficient for individual reactions could be accounted for by these falloff effects. Rate coefficient expressions for each of the key reactions were computed in modified Arrhenius form, for subsequent use in relevant kinetic models.

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# THE STRENGTH OF MODEL-BASED DESIGN FOR NITROXIDE MEDIATED POLYMERIZATION

D. R. D'hooge<sup>1,2\*</sup>, S. K. Fierens<sup>1</sup>, P.H.M. Van Steenberge<sup>1</sup>, M.-F. Reyniers<sup>1</sup>, G. B. Marin<sup>1</sup>

<sup>1</sup>Ghent University – Laboratory for Chemical Technology (LCT) Gent, B-9052 <sup>2</sup>Ghent University – Department of Textiles

Gent, B-9052

#### Abstract

Model-based design is applied for nitroxide mediated polymerization (NMP), aiming at the synthesis of welldefined macromolecules with control over chain length, composition and functionality. Attention is focused on (i) the use of multi-objective optimization to identify Pareto-optimal fronts for NMP of styrene and (ii) the controlled synthesis of poly(styrene-*b*-acrylate) block copolymers, benefiting from the explicit visualization of monomer sequences of individual macrospecies via kinetic Monte Carlo simulations. The Pareto-optimal fronts are composed of equivalent NMP process conditions from a technico-economic point of view and allow to map the full potential of NMP for a given targeted chain length and conversion. Intrinsic kinetic parameters are taken from literature or determined based on regression to an extensive set of experimental NMP data. Diffusional limitations on termination are fundamentally accounted for, which allows an accurate description of the polymerization rate and livingness as a function of polymerization time.

# Keywords

Kinetic modeling, functional polymers, model-based design.

# Introduction

Nitroxide mediated polymerization (NMP) is an important so-called reversible deactivation radical polymerization (RDRP) technique, which allows in contrast to conventional free-radical polymerization (FRP), the synthesis of polymers with high control over chain length, monomer sequences and functionality (Nicolas et al., 2013). Due to this high microstructural control advanced macromolecular architectures such as well-defined block, gradient, graft and star copolymers can be synthesized (Figure 1; Matyjaszewski (2007)).



Figure 1. Advanced macromolecular architectures accessible via nitroxide mediated polymerization (NMP); comonomer A/B: red/green sphere

The principle of NMP is given in Figure 2 (Fukuda et al., 2000). Initially an alkoxyamine initiator  $R_0X$  dissociates into an initiator radical  $R_0$  and a persistent radical X. Propagation, i.e. the addition to monomer M, subsequently occurs and macroradicals  $R_i$  are formed, which can either be deactivated into dormant polymer molecules  $R_iX$  or terminated into unwanted dead polymer molecules P.



Figure 2. Principle of nitroxide mediated polymerization (NMP); i: chain length with i=0initiator related;  $k_{a,da,p,t}$ : rate coefficient for activation, deactivation, propagation, and termination; at start: NMP initiator  $R_0X$  and monomer M; X: nitroxide and functionality in dormant form RX.

Importantly, termination inherently leads to a build-up of persistent species X and consequently deactivation is favored at higher polymerization times, allowing the synthesis of highly functional polymer molecules. This phenomenon is also known as the persistent radical effect (Fischer et al., 1997).

<sup>• &</sup>lt;u>dagmar.dhooge@ugent.be</u>

Moreover, if the NMP initiation is sufficiently fast a narrow chain length distribution (CLD) or equivalently a polymer with a low dispersity (< 1.3) results. The number average chain length at complete monomer consumption is ideally given by the initial molar ratio of monomer to NMP initiator, which is also known as the targeted chain length (TCL).

For a given comonomer pair and mediating agent, many process variables (e.g. temperature, concentrations, feeding strategy) can influence the degree of control and, hence, the process conditions should be carefully selected. This is a tedious task as often conflicting objectives are encountered, since a higher control over the polymeric microstructure is typically accompanied by an increase in the polymerization time.

In this contribution, it is demonstrated that model-guided design facilitates the identification of industrially relevant NMP process conditions to obtain a targeted polymer microstructure. Kinetic parameters are taken from literature or determined based on regression to experimental polymerization data. Attention is focused on two important NMP processes, namely the NMP of styrene with focus on control over chain length and end-group functionality (EGF) combined with a minimization of polymerization time, and the NMP of poly(styrene-b-acrylate) block copolymer, focusing on the chain extension step. For the former process, Pareto-optimal fronts are determined, whereas for the latter process advanced kinetic Monte Carlo simulations are performed to track monomer sequences of individual polymer chains and to evaluate the diblock quality.

# **Experimental procedure**

# Materials

To remove the stabilizer (4-tert-butylcatechol) styrene (Sty, monomer M,  $\geq$ 99%), Sigma–Aldrich) was passed through a column filled with basic aluminum oxide. BlocBuilder MA (NMP initiator  $R_0X$ ,  $\geq$ 99%) was kindly provided by Arkema and used as received. Tetrahydrofuran (THF,  $\geq$ 99%), Decane ( $\geq$ 99%), and dichloromethane (DCM,  $\geq$ 99%) were obtained via Sigma–Aldrich and used as received.

### Synthesis procedure

The batch isothermal NMP of styrene was performed in the presence of 6.25% (v/v, with respect to *M*) internal standard decane. A proportional-integralderivative controller was used to regulate the temperature. A broad range of TCLs (100-1000) and temperatures (90°-120°C) was investigated. Chain extension was performed at 130 °C.

#### Analysis methods

Gas-chromatography analysis was performed with a trace-GC ultra-Gas Chromatograph with a flame

ionization detector detector and a CP Wax 52 CB 30 m capillary column (275°C: injector/detector temperature; Helium flow rate: 1.3 mL min<sup>-1</sup>). In addition, the CLD was measured via size exclusion chromatography, using a PL-GPC50 plus instrument with a refractive index detector and one Resipore (50 x 7.5 mm) guard column and two Resipore (300 x 7.5 mm) columns (flow rate THF: 1 mL min<sup>-1</sup>).

# Modeling procedure

# Kinetic modeling and regression analysis

The NMP of styrene is modeled both via deterministic and kinetic Monte Carlo simulations (Van Steenberge et al., 2012), considering the reactions in Table 1. Besides conventional reactions such as propagation and termination NMP specific activation/deactivation reactions are included. Also thermal initiation, chain transfer to monomer and dimer are taken up since the model is also applied at elevated temperatures (> 100°C).

Table 1. Reactions included in the kinetic model for NMP of styrene initiated by BlocBuilder MA.

	Reaction
NMP (de)activation	
	$R_{0,1}X \xleftarrow{k_{a0}}{k_{da0}} R_{0,1} + X$
	$R_i X \xleftarrow{k_a}{k_{da}} R_i + X$
Thermal initiation	
	$2M \xleftarrow{k_d}{k_{rd}} D$
	$D + M \xrightarrow{k} R_{0,2} + R_{0,3}$
Chain initiation	
	,
	$R_{0, j} + M \xrightarrow{k p, 0 j} R_1$
Propagation	
	$R_i + M \xrightarrow{k_p} R_{i+1}$
Chain transfer	
	$R_i + M \xrightarrow{k} P_i + R_{0,4}$
	$R_i + D \xrightarrow{k} P_i + R_{0,3}$

Termination

$$R_i + R_j \xrightarrow{k_{tc}} P_{i+j}$$

For the intrinsic parameters, the reader is referred to Fierens *et al.* (2015a). Regression analysis using the Marquardt-Leverberg algorithm was used to estimate NMP activation/deactivation Arrhenius parameters while differentiating between initiator and macrospecies. For the modeling of the chain extension with *n*-butyl acrylate (nBuA), no backbiting is considered for simplicity and literature parameters are used as reported in Nicolas et al. (2013).

For termination, apparent rate coefficients are applied to account for diffusional limitations which are evoked upon an increase of the viscosity and chain length. The corresponding model parameters are taken from the work of Johnston-Hall and Monteiro (2008).

#### Calculation of Pareto-optimal fronts

The nondominated sorting genetic algorithm-II (NSGA-II; Deb et al. (2002)) is combined with the NMP deterministic model to perform multi-objective optimization with respect to time, EGF and dispersity for a given conversion of 0.75 and a TCL of 200. Optimization paths are defined for a distinct number of conversion intervals with a variation of temperature and/or reactant feed rates. A maximal polymerization time of 50 hours is allowed.

# **Results and discussion**

# NMP of styrene

Using the developed kinetic model a good description of the NMP kinetics for a broad range of polymerization conditions is obtained. The model is subsequently used to improve the control over chain length while fixing first the polymerization time and conversion. It is found that a stepwise temperature program is beneficial as it allows a lowering of the dispersity at high conversion, as shown in Figure 3 (left; red line: isothermal; purple line: stepwise temperature program; conversion: 0.7; TCL=1000).



Figure 3. Beneficial use of a temperature program for NMP of styrene (TCL=1000); left; dispersity profile with temperature program (purple) and without (red); right: classification of RX according to chain initiation with blue: R<sub>0</sub>; green: M\*; orange D\*; yellow: thermal initiation; classification of P according to termination event: red: via chain transfer to D; teal; via chain transfer to M; black: via recombination.

<sup>1</sup>For fed-batch addition, the conversion is defined with respect to the initial monomer amount of the batch case.

Moreover, with the kinetic Monte Carlo model which benchmarks with the deterministic model it is possible to understand this improvement. The monomer incorporation can be tracked per chain, including a differentiation according to chain initiation for *RX* species and termination mode for *P* species.

For example, Figure 3 (right) shows the reaction event history for a representative number of chains at a conversion of 0.70 in case the temperature program is applied. It can be seen that both dormant (bottom) and dead (top) polymer molecules are formed. The dormant ones are basically created via classical NMP initiation whereas the dead ones are not mainly formed via termination but via chain transfer to dimer. In contrast to the isothermal case less side products are obtained due to an optimized radical concentration profile inducing an optimal balance between livingness and chain initiation.



Figure 4. Pareto-optimal front for NMP of styrene at 120°C using a fed-batch monomer program with a constant molar flow rate per conversion interval of 0.125; also shown batch case; TCL=1000.

Further improvement can be obtained by allowing a broader variation of process conditions as done in the multi-objective optimization study. A typical Pareto-optimal front is depicted in Figure 4 (Fierens et al., 2015b). Here a fed-batch addition of monomer is performed with a constant molar flow rate per conversion interval of 0.125.1 For completeness also the batch case is shown. Clearly, a fed-batch program is beneficial as lower dipersities can be reached for a lower polymerization time. An even higher control over chain length is possible, although at the expense of an increase in polymerization time, due to the L-shape of the Pareto-optimal front. Alternatively, a simultaneous variation of temperature and fed-batch addition can be applied.

The shape of the front in Figure 4 can be understood by comparing the evolutions of the reaction probabilities as a function of conversion. A good control requires a low value for the ratio of the propagation to deactivation probability ( $P_{deac}/P_{prop}$ ), a low termination probability ( $P_{term}$ ), and a low chain transfer to dimer probability ( $P_{trD}$ ). Less M, as obtained during a fed-batch addition, implies a lower  $P_{deac}/P_{prop}$ and thus a more controlled incorporation of the M units. At the same times less termination occurs since the viscosity is higher and thus more diffusional limitations on termination result, which improves the EGF. In addition, a lower M concentration allows to suppress dimer formation. Hence, the negative impact of chain transfer to dimer on the control over chain length and livingness is diminished as well (see Figure 5; three representative cases of Figure 4).



Figure 5. Evolution of the chain transfer to dimer probability  $P_{trD}$  for three distinct operating points along the Pareto-optimal front in Figure 4.

### Chain extension with n-butyl acrylate

To illustrate the reliability of the kinetic model further experiments were performed aiming at a chain extension with a *n*-butyl acrylate (*n*BuA) block. Model-based design showed that each block should be synthesized at a different temperature. For example, for both blocks a respective temperature of 110 and 130°C can be selected to obtain an optimal balance between polymerization time and microstructural control.



Figure 6. Monomer sequences for chain extension with n-butyl acrylate of polymer obtained via NMP of styrene; left: first block (TCL=500; 110°C); right: second block (TCL=500; 130°C).

The corresponding monomer sequences, assuming no loss of polymer molecules during purification after the synthesis of the first block, are given in Figure 6. These sequences are again obtained by Monte Carlo simulations with the colors now referring to the monomer type, *i.e.* green for styrene and red for *n*BuA. It follows that a successful chain extension is made and most chains possess a block character.

### Conclusions

Kinetic modeling is successfully applied to perform model-based design of two important NMP processes. Lacking NMP-specific intrinsic rate coefficients are accurately determined via regression analysis, based on an extensive set of polymerization data.

Optimization can be performed particularly via multi-objective optimization with allows the identification of Pareto-optimal fronts and to map the full potential of the NMP technique. Both individual and combinatorial optimization paths can be explored with respect to control over chain length, end-group functionality and polymerization time for a given conversion and targeted chain length.

Moreover, detailed kinetic and mechanistic insights and a classification of polymers can be obtained using advanced kinetic Monte Carlo simulations in which the monomer sequences are explicitly tracked.

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gradient quality of ATRP copolymers. *Macromolecules* 45, 8519.
# DETERMINING RUBBER COMPOSITION OF WASTE TYRES USING DEVOLATILISATION KINETICS

B. Danon\*, P. van der Gryp and J.F. Görgens

Stellenbosch University - Stellenbosch Matieland, 7602, South Africa

#### Abstract

With the currently presented kinetics model of tyre devolatilisation it is possible to determine the rubber composition of a waste tyre crumb. The kinetics are based on a sophisticated devolatilisation mechanism, including two consecutive devolatilisation reactions for the rubbers, i.e. primary depolymerisation and crosslinking (condensation) of the polymers and consecutive secondary degradation of the condensed intermediate product. While it is assumed that the primary devolatilisation of the rubbers proceeds similarly as that of the rubbers separately, all the rubbers contribute to a single condensed intermediate product, which subsequently exhibits its particular degradation behaviour. The model-based kinetics (using a power-law expression for the conversion function) are solved by multivariate nonlinear regression in MATLAB. The model has been validated with ternary mixtures of three predominant tyre rubbers (natural polyisoprene, butadiene and styrene-butadiene rubber) and was subsequently applied for three waste tyre crumbs with different ratios of passenger car and truck tyres. It turned out that the model is capable of predicting the polyisoprene content very accurately. Indeed, an increasing trend in the natural rubber content for the waste tyre crumbs with increasing truck tyre content was correctly predicted. Due to the similarity of butadiene and styrene-butadiene rubber, discriminating between these two rubbers is notoriously difficult. The present model is however capable of indicating relatively high butadiene rubber contents.

#### Keywords

Rubber composition, waste tyres, devolatilisation, kinetics

#### Introduction

There are many different types and brands of tyres, which all typically consist of different rubber compositions. Once a tyre is wasted, it will be added to a waste tyre pile irrespective of its particular rubber composition. At present the main selection criterion is tyre type, separating mainly between truck tyres (TT) and passenger car tyres (PCT). Therefore, in order to use these mixtures of waste tyres for recycling purposes, the actual rubber composition is an inconvenient unknown.

There have been several previous attempts to determine the rubber composition of waste tyres using various analytical methods. These methods include TGA-DSC (Sircar & Lamond, 1973, 1975; Brazier & Nickel, 1975; Lee et al., 2007), TGA-FTIR (Fernández-Berridi et al., 2006; Lee et al., 2007), Py-GCMS (Lee et al., 2007) and TGA in combination with devolatilisation kinetics (Yang et al., 1993; Seidelt et al., 2006). All these studies indicate that it is not a straightforward exercise to obtain an accurate prediction of the rubber composition, and especially to make a distinction between the butadiene and styrene-butadiene rubber contents. Lee et al. (2007) concluded from their comparative study that Py-GCMS was the most accurate method. However, the studies using devolatilisation kinetics assume that all rubbers devolatilise fully independently. The objective of this study is to obtain the rubber composition of waste tyre crumbs using kinetics modelling of its devolatilisation employing a more sophisticated devolatilisation mechanism.

The devolatilisation kinetics of waste tyres has been extensively investigated over the last decades (Mui et al., 2004; Quek & Balasubramanian, 2012). Generally, a mechanism with three independently reacting (pseudo)components has been assumed (Mui et al., 2008; Aylón et al., 2005; Leung & Wang, 1999; Conesa et al., 1997; Kim et al., 1995), while some studies included consecutive reactions (Cheung et al., 2011), parallel reactions of single pseudocomponents (Mui et al., 2008) or elastomersimulation as the pseudocomponents (Leung & Wang, 1999). Although the results of the application of these more advanced devolatilisation mechanisms were promising, they have not yet been ap-

<sup>\*</sup>To whom all correspondence should be addressed: bdanon@sun.ac.za.

plied for the prediction of rubber contents in waste

tyres. Model-based kinetics, with a power-law function as the conversion function, are mostly employed (Cheung et al., 2011; Mui et al., 2008; Aylón et al., 2005; Conesa et al., 1997; Leung & Wang, 1999). Model-free isoconversional methods have been implemented more sparingly for waste tyre devolatilisation kinetics (Kim et al., 1995; Teng et al., 1995)

This paper consists of three parts. First the

devolatilisation mechanism and kinetics modelling approach is presented. Subsequently, this model is validated with experimental results of ternary rubber mixtures with known compositions of natural rubber (NR), butadiene rubber (BR) and styrenebutadiene rubber (SBR). Finally, the model is applied to three waste tyre crumbs with different TT to PCT ratios.

#### Experimental

Natural rubber (SMR 20) was sourced from Continental Tyre SA, while the 97% cispolybutadiene rubber (Neodene 40) and the cold emulsion polymerised styrene-butadiene random copolymer (Afpol 1500, 23.5% styrene) were both procured from a local rubber manufacturer (Karbochem). The rubbers have been cryogenically milled in order to obtain a particle size below 1 mm, but other than that were used as received. Three different tyre crumbs (all with mesh size 40) were obtained from three different local tyre recycling companies (Dahwi Rubber Recycling, SA Tyre Recyclers and Goswell Developments) and used as received.

A Mettler Toledo TGA/DCS 1 analyser was used for the kinetics experiments. For the ternary validation experiments samples were prepared to be 12 mg, while for the experiments with the crumbs a sample size of 10 mg was used. The thermogravimetric program consisted of a drying period of 5 min at 110 °C, followed by the kinetics experiment up to 600 °C at constant heating rate and nitrogen flow of 100 mL min<sup>-1</sup>. It is assumed that at these particle sizes and heating rates mass and heat transfer limitations will be negligible (Quek & Balasubramanian, 2009).

#### Kinetics model

The following devolatilisation mechanism is assumed for the kinetics modelling, see Figure 1. The waste tyre crumb particle consists of three main constituents, i.e., a filler, chemical additives and the rubber mixture. First, it is assumed that the the inert filler (generally carbon black) includes

most of the ash and is not influencing the rubber devolatilisation (Kleps et al., 1990). The chemical additives evaporate separately from the rub-

bers to volatiles at lower temperatures. Finally,



Figure 1. Devolatilisation mechanism of a waste tyre crumb particle. A = Additives, CB = Carbon black, NR = Natural rubber, BR = Butadiene rubber, SBR= Styrene-butadiene rubber, ICP = Intermediate condensed product.

the devolatilisation of the rubbers proceed via two consecutive devolatilisation reactions, i.e., primary depolymerisation (simultaneously with crosslinking) of the polymers and consecutive secondary degradation of the intermediate condensed product (Danon et al., 2015). While it is assumed that the rubbers depolymerise independently, they all contribute to a single intermediate condensed product. The ratios of weight involved in these two different devolatilisation reactions for each rubber were taken from experiments with the individual rubbers (Danon et al., 2015). The other weight fractions, i.e. that of the additives and the three rubbers in the tyre matrix, are estimated in the present model. For the evaporation reaction of the additives (R1) and the rubber depolymerisation reactions (R2-R4) previously determined kinetics parameters are used (Danon et al., 2015). It is further argued that the intermediate condensed product (ICP), which originates from crosslinking (condensation) of the polymer radicals during depolymerisation, is a mixed product of all the three rubbers, since these reactions cannot be assumed to be selective for any type of rubber. Therefore, a different ICP is formed for every individual tyre (with specific rubber composition) and a full set of kinetics parameters (E, A and n) were estimated for the degradation reaction R5. Thus, although a sophisticated devolatilisation mechanism is employed, only six parameters had to be estimated, i.e., the E, A and n of the degradation reaction and the weight fractions  $(\gamma)$  of the additives and of two of the three rubbers (the last is calculated by difference).

The applied model-based kinetics are similar to those used for the separate tyre rubbers (Danon et al., 2015). This model entails a multivariate non-linear regression method of the solid-state Arrhenius rate of change of the conversion,

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \mathrm{A} \, \exp \, -\frac{\mathrm{E}}{\mathrm{RT}} \, (1-\alpha)^{\mathrm{n}} \tag{1}$$

where  $\alpha$  represents the conversion (-), t time (s),



Figure 2. Measured and modelled derivative thermogravimetric (DTG) data of (a) Dawhi, (b) SATR and (c) Goswell waste tyre crumb at 10  $^{\circ}C$  min<sup>-1</sup>. Subscript mod indicates the modelled data and the numbers coincide with the

reactions indicated in Figure 1.

A the pre-exponential factor  $(s^{-1})$ , E is the activation energy  $(J \text{ mol}^{-1})$ , R the universal gas constant  $(8.314 \text{ J} \text{ mol}^{-1} \text{ K}^{-1})$ , T the temperature (K) and  $(1 - \alpha)^n$  is the conversion function, with n as the reaction order (-). The total change in conversion is then,

$$\frac{d\alpha}{dt} = \gamma_{A} \frac{d\alpha_{A}}{dt} + (1 - \gamma_{A}) \sum_{i=1}^{N} \gamma_{i} \gamma_{i,1} \frac{d\alpha_{i,1}}{dt} + (1 - \gamma_{A}) \sum_{i=1}^{N} \gamma_{i} \gamma_{i,2} \frac{d\alpha_{2}}{dt}$$
(2)

where i represents the ith rubber of a total of N rubbers and the subscript A, 1 and 2 indicate the additives or the fraction of the rubbers that devolatilise via primary depolymerisation and secondary degradation, respectively. Note that the three main terms in Equation 2 coincide with the evaporation, depolymerisation and degradation reactions as indicated in Figure 1, respectively. Finally, the sum of squared normalised errors is used for the minimisation.

The activation energy E of the degradation reaction is determined separately using the Friedman method, a differential model-free isoconversional technique (Friedman, 1964). The natural logarithm of each side of Equation 1 results in the following expression,

de

$$\ln \frac{d\alpha}{dt} = \ln [A f(\alpha)] - \frac{E}{RT}$$
(3)

for which it is assumed that the conversion function  $f(\alpha)$  is merely dependent on conversion and thus independent of temperature. A plot of  $\ln [d\alpha/dt]$  versus 1/T at a fixed value of the conversion will result in a straight line with slope E/R. The values of the apparent E are calculated with this method for constant values of the conversion between 0.01 and 0.99 with intervals of 0.01 and the value of E

The kinetics model is solved using MATLAB R2014a and the strategy was as follows. First, a initial guess for the pre-exponential factor A was chosen such that the peak of the degradation reaction is close to the measured peak with an initial guess for the reaction order of unity. Next, the initial guesses for both A and n were varied around

the values predicted by this initial run. Then, the solution with the lowest sum of squared errors was taken as the final solution. For the models of

the tyre crumbs the initial guesses for the rubber weight fractions were taken as equivalent amounts of each rubber.

#### **Results and Conclusions**

From the validation experiments it was observed that the predicted NR contents are very accurate, while the model tends to overpredict the SBR content if the total synthetic rubber content (BR + SBR) was relatively low. It seems that BR in a rubber mixture behaves more like the butadienepolymer segments in SBR. In Figure 2 the measured and modelled derivative thermogravimetric (DTG) data of the devolatilisation of the three rubber crumbs are presented. It can be observed that the model is well capable to reproduce the measured data. Moreover, the model correctly predicted higher NR contents for the crumbs with higher percentages of TT.

It is concluded that the use of a kinetics model which is based on a sophisticated devolatilisation

at a conversion coinciding with the maximum in the derivative thermogravimetric curve during secondary degradation is used in the kinetics model. mechanism, incorporating interactions between the devolatilisation of the individual rubbers, significantly improved the predicting capability of this analytical approach. In the context of producing valuable chemicals from waste tyre by pyrolysis, e.g. dipentene which derives from the NR content, the present characterisation method will prove very useful.

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# AUTOMATIC KINETIC CALCULATIONS FOR REACTION MECHANISM GENERATION

Pierre L. Bhoorasingh<sup>\*</sup> and Richard H. West Northeastern University Boston, MA 02115

Keywords

Transition State Theory, Reaction Mechanism, Rate Estimation.

Automated mechanism generators build detailed kinetic models that contain many thousands of intermediate reactions and species. Kinetic and thermodynamic parameters are needed to fully describe the model, but as data are scarce most of these parameters are estimated, for example using Benson's group additivity. Accuracy suffers when systems differ from those used to train the estimates. We present an automatic algorithm to calculate kinetic parameters via quantum chemistry and transition state theory for use with an automated mechanism generator.

Reaction Mechanism Generator (RMG)<sup>1</sup> includes an automated algorithm for calculating thermodynamic parameters via semi-empirical quantum chemistry calculations, which improves modelling of systems containing fused-ring species<sup>2</sup>. In our related approach for kinetics, interatomic distances at the transition state (TS) are first estimated via a group contribution method, allowing TS geometry estimates to be created using distance geometry. The geometry estimate is optimized by commercially available quantum chemistry packages, then automatically validated by an intrinsic reaction coordinate calculation and graph matching. The CanTherm package<sup>3</sup> calculates the reaction rate using optimized geometries of the TS, reactants, and products. Our algorithm will reduce kinetic parameter uncertainty, and is currently being tested on a diisopropyl ketone combustion model<sup>4</sup>, previously built using RMG.

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## Implementation of stereochemistry in automatic kinetic model generation

Nick M. Vandewiele<sup>b</sup>, Ruben Van de Vijver<sup>a</sup>, Kevin M. Van Geem<sup>a\*</sup>, Marie-Françoise Reyniers<sup>a</sup> and Guy B. Marin<sup>a</sup>

<sup>a</sup> Laboratory for Chemical Technology, Universiteit Gent, Technologiepark 914, 9052 Ghent, Belgium

<sup>b</sup> Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

#### Abstract

This work discusses the extension of an existing network generation tool, called Genesys, by accounting for stereochemistry in kinetic models. Genesys was extended by the addition of algorithms for the detection of stereocenters, and for the identification of stereoisomers. To that purpose a so-called 2.5D representation of molecules that accounts for the presence of stereocenters and that keeps track of the associated stereoconfiguration of the stereocenters is introduced. A novel algorithm for the detection of steric relations between substituents allows the automated assignment of rate coefficients to stereoselective reactions. The functionality of the tool is illustrated for the thermal rearrangement of the monoterpenoid 2-pinanol, in which accounting for the stereochemistry is crucial to explain the reactive behavior of 2-pinanol and its products. Good agreement with experimental data was obtained.

#### Keywords

Automatic kinetic model generation, stereochemistry, pinanol thermal rearrangement.

#### Introduction

During the last decades, new applications involving stereochemistry, such as asymmetric synthesis of pharmaceuticals and agrochemicals (Noyori, 2002), and conversion processes of natural products such as terpenes (Corma et al., 2007) emerged for which the characterization of stereochemistry is required to understand the reactivity of the molecules. In this context, computer-aided modeling of these chemical processes requires an adequate representation of stereochemistry in order to capture the essential characteristics of the chemical process. A valuable tool to study chemical processes are kinetic models, which give quantitative insights in the product distribution as a function of reaction conditions. For many chemical processes manual construction of kinetic models is no longer possible because of their complexity. To cope with this, computers were programmed to automatically generate kinetic models (Ratkiewicz and Truong, 2006; Pierucci and Ranzi, 2008; Battin-Leclerc et al., 2011). Many tools have been proposed to automatically create kinetic models (Warth et al., 2000; Vandewiele et al., 2012; Green et al., 2013), but none of them account for stereochemistry. The reason for the lack of support for stereochemistry in the generated kinetic models was and is the underlying representation of molecules in these codes. Molecules are often represented as mathematical graphs, in which the nodes of the graph represent atoms, and the edges represent bonds. By doing so, a plethora of graph-theoretic algorithms and solutions have been proposed and implemented to accomplish tasks such as identification of species uniqueness, substructure searching, greatly facilitating the efforts of extracting knowledge from chemical data by means of computers. Unfortunately, the graph representation also implied that the characterization and manipulation of stereochemical features of molecules and reactions became impossible since graphs only represent the connectivity between

atoms, and not the arrangement in the three-dimensional space.

This work discusses the necessary steps to automatically create kinetic models that account for stereochemistry. The functionality of the new tool is illustrated for the thermal rearrangement of the monoterpenes cis- and trans-2-pinanol. A kinetic model is constructed for this chemical process that accounts for the stereochemistry and is compared to experimental data obtained from literature.

#### Methodology

Genesys (Vandewiele et al., 2012) is a tool for the automatic generation of kinetic models, consisting of a reaction network containing molecules and elementary reactions together with thermodynamic and kinetic data. The reaction network is generated by the iterative application of a limited set of reaction families that convert reactant molecules into product molecules. A pool of species, e.g. the reactants of a chemical process, is used to initiate the network generation and the species list is continuously extended with species that arise as products of elementary reactions.

For kinetic models that want to take into account stereochemical effects, a number of additional aspects need to be considered. First of all, the data structures designed to represent molecules inside the network generation code should allow distinguishing between stereoisomers. Information on stereochemical aspects of molecules needs to be correctly converted from the user interface into an internal molecule representation, and vice versa. Alternatively, if the user specifies a reactant in which the absolute configuration of the stereocenters is not uniquely defined, Genesys identifies these stereocenters through an adequate stereocenter detection algorithm, and exhaustively generates all possible stereoisomers using a so-called stereoisomer generation algorithm.

Secondly, continuous updating of stereocenters in reactant stereoisomers is needed

because of the formation of new stereocenters in product stereoisomers may arise in the course of the network generation. Furthermore, a reaction may lead to multiple distinct stereoisomers. The same stereocenter detection algorithm and stereoisomer generation algorithm used for the exhaustive generation of all stereoisomers corresponding to the reactant structure is now used to handle the newly created products of a reaction.

Finally, reactions may be stereoselective or stereospecific. Stereoselectivity refers to the preferential formation of or the other of two (or more) stereoisomers from a single molecule with a prostereogenic element (Eliel, 1962). The latter refers to an element that can be converted from nonstereocenter to stereocenter in a single step (McNaught and Wilkinson, 1997). Stereospecificity refers to the difference in reaction rates of two stereochemically different molecules, i.e. diastereomers or enantiomers (Eliel, 1962). The stereospecificity of a reaction is sometimes linked to the absolute stereoconfiguration of stereocenters and is explained by the lock-and-key specificity of catalysts such as enzymes. Stereoselectivity depends on the differences in free energies of the respective transition states and is explained by stereoelectronic and steric factors among others.

An algorithm is constructed that identifies the steric relation of substituents in molecules allowing the introduction of stereoselective and stereospecific rate coefficients for a reaction. After a reaction creates the product structures, containing newly created stereocenters with unspecified absolute configurations, the stereoisomer generation algorithm determines the possible stereoisomers. If the user disposes of information on the stereoselectivity or stereospecificity of a reaction family, Genesys allows the assignment of distinct rate coefficients for these reactions, based on the steric relation between the user-specified substituents. Once the steric relation between the designated substituents of the product or reactant stereoisomers is detected, prefixes such as *cis* and *trans* can be assigned to the different reactants or products. For each of the elementary reactions that convert a reactant into a possible stereoisomer a distinct rate coefficient is assigned, which is determined by the steric relation that is detected in the previous step. The rate coefficient that is associated with a particular steric relation is retrieved from the user-defined reaction family definition.

#### Pinanol rearrangements

The method and implementation of kinetic model generation incorporating stereochemistry is demonstrated and validated for the thermal rearrangements of the monoterpenoid 2-pinanol, shown in Figure 1.This compound belongs to the terpenoids, a highly diverse and functional class of biomassderived isoprene oligomers. 2-pinanol is heavily used in the fragrance, flavor and pharmaceutical industry (Mercier and Chabardes, 1995; Nowicki, 2000; Swift, 2004; Corma et al., 2007). The thermal rearrangement of 2-pinanol is an important industrial production route for linalool, also depicted in Figure 1, used in perfumes and as a precursor for vitamins A and E (Mercier and Chabardes, 1995).



Figure 1: Structures of 2-pinanol and linalool.

There are four stereoisomers of 2-pinanol. They relate to each other as two pairs of diastereomers, depending on the spatial arrangement of the dimethyl bridge relative to the hydroxyl group. Each pair of diastereomers relates to each other as enantiomers. Previous work (Vandewiele et al., 2011) showed that significant differences in pyrolysis reactivity and selectivity could be observed between the two diastereomeric pairs. Furthermore, distinguishing between the enantiomers of linalool is important because each enantiomer has distinct odor characteristics and thresholds (Ohloff and Klein, 1962; Fritsch and Schieberle, 2005). The structures of the product species arising during the pyrolysis of 2pinanol are shown in Figure 2.



Figure 2: Chemical structures of compounds involved in the thermal rearrangement of 2-pinanol: 1: 2-pinanol, 2: linalool, 3: 6-terpineol, 4: 1,4-disubstituted cyclohexanol biradical, 5: 1,2-disubstituted cyclohexanol biradical, 6: isolinalool, 7: plinol, 8: isoplinol, 9: 5,7-dimethyloct-6-ene-2-one.

The procedure of the automated kinetic model construction proceeds as follows: 2-pinanol is specified as reactant using a species identifier such as an InChI without specifying the absolute configurations of the stereocenters. The stereoisomer generation algorithm generates four distinct structures. The reaction pathways that are relevant for the thermal decomposition of 2-pinanol were described in detail in previous work (Vandewiele et al., 2011). The chemical knowledge on the relevant pathways involved in the thermal rearrangement of 2-pinanol is translated into reaction families. Four reaction families are defined: homolytic C-C scission reactions, biradical β-scission reactions, sigmatropic [1,5]-H-shift reactions and enecyclization reactions. The fragmentation of the fourmembered ring by homolytic C-C scission reactions is the initial step in the thermal isomerization of bicyclic monoterpenes consisting of a bicyclo[3.1.1]heptane system. This scission reaction leads to four 1,4disubstituted cyclohexanol biradicals. The 1,4disubstituted biradicals quickly rearrange into linalool enantiomers through C-C β-scission reactions involving the bond in  $\beta$ -position of the two carbon atoms bearing the unpaired electron. An alternative, minor pathway leads  $\beta$ -terpineol, via sigmatropic [1,5]-H-shift reactions. Linalool further isomerizes into plinol products via pericyclic ene-cyclization reactions. Note that the application range of a reaction family needs to be constrained as much as possible so only molecules are considered that can react based on this reaction type.

The calculation of thermochemical properties and symmetry numbers of the species in the model follows the same methodology as described in previous work (Vandewiele et al., 2012; Vandewiele et al., 2014). The assignment of the rate coefficients to each elementary reaction occurs on the level of reaction families in Genesys. Ideally,  $\Delta GAV^\circ s$  obtained from ab initio calculations are used to calculate values for the rate coefficients of the generated reactions. Unfortunately, values for  $\Delta GAV^{\circ}s$  for the reaction families required for the thermal decomposition of 2pinanol are unavailable. Instead, fixed Arrhenius parameters were used for the generated reactions of each reaction family, derived from experiments. The provided pre-exponential factor for a reaction family is a single-event pre-exponential factor that is multiplied by the number of single-events of that particular reaction. The number of single-events is calculated following the algorithm described by Vandewiele et al. (Vandewiele et al., 2014).

The activation energy of the rate coefficient of the homolytic C-C scission reactions of 2-pinanol is 5 kJ mol<sup>-1</sup> lower when the methyl group of the chiral carbon atom is in *cis* position relative to the dimethyl bridge of the bicyclo[3.1.1]heptane system, compared to *trans*-structure in which the methyl group is in *trans* position relative to the dimethyl bridge. For the homolytic C-C scission reactions, the influence of the arrangement of the methyl group next to the chiral carbon with respect to the dimethyl bridge on the rate coefficients is added as a further specification to the reaction family. The steric relation detection algorithm enables the automatic assignment of the appropriate rate coefficient for the corresponding stereoisomer.

Similarly, rate coefficients were also derived for the  $\beta$ -scission reactions, the H-shift reactions, and the ene-cyclization reactions (Vandewiele et al., 2011).

#### **Results and discussion**

The generated kinetic model for the thermal rearrangement of 2-pinanol consists of only 20 elementary reactions between 20 species. The presented kinetic model is an improvement of the kinetic model of Vandewiele et al. (Vandewiele et al., 2011) on 3 levels. First, this new kinetic model is automatically constructed, as opposed to the previous model that was constructed by hand. Second, the new kinetic model distinguishes between enantiomers while the hand-built model lumps them together. Last but not least, the model presented in this chapter accounts for the stereoselectivity of the ene-cyclization of linalool, by incorporating distinct reactions to each of the stereoisomers of plinol. The previously build model only provides a lumped reaction in which a global reaction rate is provided towards the lumped plinol isomers.

The predictions of the generated kinetic model are compared against experimental data by Leiner et al. (Leiner et al., 2013). The reactor in the experiments consists of a 200 mm long quartz tube with a diameter of 15 10-3 m. 5000 ppm of the reactant was fed to the setup in a N<sub>2</sub> flow at temperatures between 623 and 873K and a pressure of 1bar. Conversions ranging from 0 to 100% were obtained with these conditions. Species at the reactor outlet are identified and quantified using GC-FID and GC-MS. Simulations were carried using the plug flow reactor model of the Chemkin 4.1 package (Kee et al., 2007), using the reported reactor dimensions and conditions.



Figure 3: Mole fraction as a function of reactor tempearture of a) 2-pinanol, b) linalool, c) sum of isomers of plinol. Model predictions: cis-2-pinanol as feed (blue, full lines), trans-2pinanol as feed (red, dashed lines). Experiments: cis-2pinanol as feed (blue, full symbols), trans-2-pinanol as feed (red, hollow symbols).

Figure 1 shows the mole fractions as a function of the reactor temperature for 2-pinanol, linalool and plinol for experiments with cis- and trans-1 as the feed. Since the feed was not enantiomerically pure, the mole fractions of enantiomeric species in the model were lumped together and the sum of the mole fractions of both enantiomers for the experiments and the model predictions was compared instead. Also,

measured concentrations of minor products were not reported, and thus could not be used for comparison. The conversion of both diastereomers of 2-pinanol is slightly overestimated, resulting in a small overestimation of the mole fractions of linalool. Overall, good agreement was found between model and experiment, especially given that none of the parameters in the model were fitted to the experimental data.

#### Conclusion

This work presents the extension of Genesys for the automatic construction of kinetic models for molecules and reactions that account for stereochemistry. It uses a 2.5D representation of molecules, i.e. a graph representation augmented with so-called stereoparities for the stereocenters of the molecules. Genesys keeps track of the absolute configurations of existing stereocenters, the creation or destruction of stereocenters, and the generation of stereoisomers.

The functionality of the tool was illustrated by the automated construction of a kinetic model for the thermal rearrangement of 2-pinanol. Using a stereoisomer generation algorithm, the four existing stereoisomers of 2-pinanol were generated from a structure in which the absolute configuration of the stereocenters was not specified. The trans-linked pinanol isomers were identified using the methodology for the detection of the relative arrangements of substituents of stereocenters. Four reaction families were defined and used to generate the kinetic model for 2-pinanol. The model was validated using experimental data from literature and showed the good agreement between the model predictions and the measured concentrations of the reactant and products without adjustment of any of the reaction rate coefficients.

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## Improving kinetic models for alcohol combustion: an iso-butanol case study

Samah Y. Mohamed<sup>1</sup>,\*, Shamel S. Merchant<sup>2</sup>, Nathan Yee<sup>2</sup>, William H. Green<sup>2</sup> and S.M. Sarathy<sup>1</sup> <sup>1</sup>King Abdullah University of Science and Technology, Thuwal - Saudi Arabia

<sup>2</sup>Massachusetts Institute of Technology, Cambridge - United States

#### Abstract

n-Butanol and its isomers have higher energy density and are more compatible with engines compared to traditional alcohol-based biofuels (e.g., ethanol). Therefore, a fundamental understanding of butanol combustion chemistry is addressed in this study. A comprehensive analysis of the recent detailed low and high-temperature iso-butanol models by Sarathy et al. (2012) and Merchant et al. (2013) has been performed. This is to provide a better understanding of alcohol combustion behavior and to give insights into the most important reactions that should be given more attention theoretically or experimentally.

#### Keywords

Iso-butanol, chemical kinetic modeling, thermochemistry, alcohol combustion.

#### Introduction

Recent concerns about environmental issues have raised the importance of replacing fossil fuels, especially petroleum fuels. These alternative fuels should maintain the same benefits as conventional fuels, such as low cost and high energy density, while securing a continuous supply with less environmental impact (Weber and Sung, 2013). Biofuels are identified as important alternative fuels. Particularly, ethanol is one of the most widely used biofuel, despite being produced from food sources and also exhibiting some combustion inefficiencies (Weber and Sung, 2013). Butanol and its isomers overcome these issues by having higher energy density and being more compatible with engines compared to traditional alcohol-based biofuels (e.g., ethanol). Moreover, isobutanol has a higher octane number compared to nbutane, which makes iso-butanol a good potential for blending with gasoline (Sarathy et al., 2012).

In this study, two detailed low and high temperature iso-butanol models by Sarathy et al. (2012) and Merchant et al. (2013) were used to analyze alcohol combustion chemistry. Sarathy et al. (2012) developed and validated a rate rule based chemical kinetic model for all four butanol isomers. Merchant et al. (2013) developed an automatically generated model using the Reaction Mechanism Generator (RMG) software package. Although, both mechanisms are well validated, a study by Weber and Sung (2013) showed that both mechanisms showed a remarkable deviation from an RCM ignition data at 30 bar, while Sarathy et al. (2012) mechanism agreed well at a lower pressure of 15 bar. Weber and Sung (2013) attributed this disagreement to the strong peroxy chemistry (especially  $\alpha$ -hydroxybutylperoxy) involved in Sarathy et al. (2012) model in contrast to Merchant et al. (2013) model.

The present study investigated thermodynamic data, species profiles, rate of productions, and ignition delay times to identify more sources of discrepancy in the two models. Different thermochemical and kinetic estimates indicated the need for more certainty in the available calculated and measured data used to develop alcohol combustion models. Further analyses of reaction paths and sensitivities were conducted to determine the most important reactions in and at transition between the two sub-stages of single-stage ignition.

#### Thermodynamic data:

The thermodynamic data of both models is estimated based on Benson's group additivity method (Benson and Buss, 1958). However, thermodynamic properties in the Sarathy et al. (2012) model were recalculated using recent group values updated and optimized by Burke et al. (2015). A comparison between the two models showed a deviation up to 4Kcal in H<sub>f</sub>, 8Kcal in S<sub>o</sub> and 5Kcal in C<sub>p</sub>, of some low temperature species. This is because most of the updated groups were low temperature groups such as OO/C/H and ALPEROX (Burke et al., 2015). This discrepancy should be considered carefully in any further rate comparisons, as most of the Merchant et al. (2013) rates are written in the reverse direction. Hence, the thermodynamic data will be used by reacting flow solvers to estimate forward reaction rate.

#### Species profile:

Prior to model comparisons, the fuel abstraction by OH was updated in both models using McGillen et al.'s (2013) proposed rates.

A comparison of the major species was conducted at 800 K and 40 atm. Species profiles (See Figure 1) with both models indicated single-stage ignition for iso-butanol, in contrast to alkanes. However, the single stage ignition can be deconstructed to two distinct sub-stages. In the first sub-stage, the radical pool concentration, especially OH and HO2, increases exponentially at very short times. In the second sub-stage, radical concentrations increase at a slower rate up to the point of ignition. The second sub-stage extends for a longer period of time, making the reactions in this sub-stage more important in controlling ignition. However, the two models showed different slopes in the early times of the first sub-stage (less than 1 micro sec), which is attributed to the difference in the Fuel+O2 initiation reaction rates. Updating this reaction class rate rule in the Merchant et al. (2013) model resulted in nearly identical features as the Sarathy et al. (2012) model in the first sub-stage. On the other hand, a steeper slope of the second substage in the Sarathy et al. (2012) model is observed, which is due to the important pathways leading to ketohydroperoxides included in the Sarathy et al. (2012) model and not in the Merchant et al. (2013) model. This motivated forcing RMG to include ketohydroperoxides pathways in order to eliminate some uncertainty in further comparisons between the models.



Figure 1: Species profile at 800K, 40 atm and phi=1. Sarathy model (dotted line) and Merchant model (Solid line). 1 indicates the 1<sup>st</sup> sub stage. 2 and 3 indicate the 2<sup>nd</sup> sub stage for Sarathy and Merchant models, respectively.

#### Ignition delay time:

The ignition delay time is also compared against RCM data from (Weber et al., 2013) The Sarathy et al. (2012) model showed better agreement as shown in figure 2. However, further investigation is required to explain the  $O_2$  pressure dependent behavior in the Sarathy et al. (2012) model. The Merchant et al. (2013) model overestimates the ignition delay especially at low equivalence ratio.

#### Flux analysis:

A detailed flux analysis shows the important reaction pathways of  $\alpha$ ,  $\beta$ , and  $\gamma$  iso-butanol radicals, as represented in figure 3 (where  $\alpha$ ,  $\beta$ , and  $\gamma$  refers to a radical in the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> carbon away from the OH moiety). The fluxes are calculated based on the species rate of production (ROP) at phi=1, 800K and 20% consumption of the fuel. The ROP shows that the major pathway of fuel consumption is by H-atom abstraction by OH and HO2 leading to the  $\alpha$ -radical. This pathways is favored since the  $\alpha$  C-H bond is the weakest relative to  $\beta$  and  $\gamma$  C-H bonds (Sarathy et al., 2012). The two models showed quite different fluxes in the subsequent  $\alpha$ -radical reactions, whereas a good agreement is found for  $\beta$  and  $\gamma$ -radicals. This disagreement is attributed mainly –as mentioned earlier- due to the strong hydroxybutylperoxy chemistry in Sarathy et al. (2012) which further leads to the low temperature chain branching reaction. On the other hand, 99% of  $\alpha$ -hydroxybutylperoxy terminates to form methyl-propanal+HO2 in the Merchant et al. (2013) model; the remaining 1% following low temperature pathways are not fully developed by RMG. This is because species produced in low fluxes (relative to a specified threshold) are ignored by RMG.



Figure 2: Ignition delay time at 30 bar, phi=0.5 (Black) and 2 (Gray), Sarathy model (dotted line) and Merchant model (Solid line)

#### Conclusions

The performance of two detailed chemical kinetic models of iso-butanol combustion has been investigated in this research. The models showed a qualitative agreement in the species profile by showing single-stage ignition with two sub stages. However, differences in the detailed low temperature chemistry and thermodynamic data between the two models resulted in discrepancies in some combustion properties, such as ignition delay times and species fluxes.

In order to assure the two models include all the potentially important reaction pathways, the Merchant et al. (2013) model will be modified to include all low temperature pathways. Furthermore, sensitivity and ROP analysis at the first and second sub stages will then be carried out. This will determine the most sensitive reactions, and provide directions for more experimental and computational efforts on rate estimation.

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Figure 3: Flux analysis at 800K and 40 bar

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# AramcoMech: a hierarchal chemical kinetic model for hydrocarbon fuels

Amer Amer<sup>1</sup>, Ali Dawood<sup>1</sup>, Henry J. Curran<sup>2</sup>, Frederique Battin-Leclerc<sup>3</sup>, Craig Taatjes<sup>4</sup>, S. Mani Sarathy<sup>5</sup>

 Research & Development Centre, Saudi Aramco, Dhahran 31311, Saudi Arabia
 Combustion Chemistry Centre, National University of Ireland, Galway, Ireland
 Laboratoire Réactions et Génie des Procédés, Université de Lorraine, CNRS, ENSIC, France
 4 Combustion Research Facility, Sandia National Laboratories, Livermore, USA
 5 Clean Combustion Research Center, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia

#### Keywords

Chemical kinetic modeling, reaction mechanisms, natural gas combustion, jet stirred reactor, photoionization mass spectrometry

The transportation sector is a major consumer of today's world energy and a major producer of carbon dioxide emissions. Because transportation vehicles rely dominantly on combusting hydrocarbon fuels to provide the necessary energy propulsion, the efficiency of the combustion process is of immense importance to the reduction of transportation energy consumption and carbon emissions. Researchers around the world are continuously investigating possible ways to improve this efficiency, and the computational modeling of the combustion process has proved to be a helpful tool in this very challenging endeavor. The modeling of combustion relies on understanding the complex chemical reaction, thermodynamic, and transport interactions during the combustion process. These interactions are normally represented by a model called a chemical kinetic model, comprising a reaction kinetics mechanism with associated species thermodynamic and transport data.

Saudi Aramco, realizing the importance of combustion modeling and the existing deficiencies, embarked on a major initiative to advance the knowledge of combustion chemistry through development of improved kinetic models for hydrocarbon fuel oxidation. The initiative was formed under the Kinetics Cluster of Excellence with researchers from Sandia National Labs in the U.S., CNRS-Nancy in France and NUI-Galway in Ireland. Following the success of the Kinetics Cluster of Excellence, Saudi Aramco formed the FUELCOM program with the Clean Combustion Research Center at King Abdullah University of Science and Technology. In this presentation, we discuss the development of an improved chemical kinetic model for the oxidation of small hydrocarbons ranging from C<sub>1</sub> to C<sub>4</sub>. The "AramcoMech" is developed primarily through collaboration with our partners at NUI-Galway. The chemical reactions of these base components constitute a central building block in understanding the combustion characteristics of practical fuels, particularly in emerging transportation combustion technologies, such as low temperature combustion engines. The mechanism has been validated against experimental data over a wide range of conditions and idealized configurations, including shock tubes, rapid compression machines, premixed flames, perfectly stirred reactors, and laminar flow reactors. An extensive comparison with previously developed kinetic models revealed significant improvement in simulating experimental measurements. The discussion describes the improvements in this mechanism and shows their significance in advancing our understanding of fuel combustion in real life applications, especially in future transportation engines.

# CHARACTERIZING IGNITION BEHAVIOR THROUGH MORPHING TO GENERIC CURVES

Edward S. Blurock<sup>1</sup> <sup>1</sup>REACTION, Lund, Sweden

#### Abstract

The qualitative notion that ignition processes have similar behavior, even over an extensive range of starting conditions, is quantitatively demonstrated through the production of a single 'generic' ignition curve. The key to the production of the generic curve is the recognition that the basic shapes of the species and temperature profiles occurring in the ignition process differ only in their 'timing'. By 'morphing' the time scale, the profile shapes can be made to align. From the aligned profile shapes a generic or 'average' profile can be derived. Synchronizing chemical events modifies the ignition progress times. In addition to fixing the ignition time to have the progress value of one, intermediate ignition events (such as selected profile maxima or inflection points) that occur before ignition are also aligned to have specific 'normalized' times.

#### Keywords

Ignition, combustion, combustion regimes, combustion mechanism, generic curves

#### Introduction<sup>1</sup>

Within a given parametric range (i.e. ranges of starting temperatures, pressures and equivalence ratios), which can be quite extensive, the behavior of an adiabatic homogeneous zero-dimensional constant volume (or pressure) process is quite regular. The process goes through several well defined regimes, for example initiation, build-up of radicals, ignition and finally equilibrium(Blurock, 2006, 2004). The curves in Figure 1 show that the behavior is similar regardless of the starting conditions (Griffiths and Barnard, 1998). The only real differences are when the events occur, for



Figure 1: A set of ignition curves for ethanol at different starting conditions. The time versus temperature plot for 5 starting temperatures and three different equivalence ratios. The solid, dotted and dashed lines are for the equivalence ratios, 0.5, 0.75 and 1.0, respectively.

<sup>1</sup> Corresponding Author:

edward.blurock@esblurock.info

example ignition time, and exact values, for example the maximum values of species mass fractions. Exploiting these similarities is the basis of all kinetic reduction (Tomlin and Turányi, 2013). The prerequisite is that the mechanistic steps within the parametric ranges are similar. Within other ranges, with other mechanisms at work, another set, similar of similar behavior would be observed.

#### Morphing to a single generic curve

A major purpose of this paper is to give a quantitative algorithm to substantiate the intuitive notion of general ignition behavior. This general behavior is represented by a generic curve. This work exploits the similarities of an ignition process to produce generic ignition curves, uniting ignition curves, each with different starting conditions, into one common behavior using one single progress variable. The inherent assumption is that a given progress value, regardless of its origin, should represent a given stage of the ignition process. In terms of species profiles, for example, this means that a given species reaches a maxima at the same progress value regardless of starting conditions. The creation of a single generic ignition curve (one for each species and two more for temperature and pressure) from a range of starting conditions is substantiation of the intuitive notion that the ignition process is going through the same set of mechanistic steps. Another range of parameters might represent another set of mechanistic steps and would be represented with another set of generic curves.

This paper, dealing with zero dimensional auto-ignition curves, performs a normalization process, similar to curve morphing (though usually associated with more complex objects (Alexa, 2002)) or conformal mappings (or a variety of other standard coordinate transformations). A transformation, through stretching and shrinking, of coordinates is used to produce a single generic curve valid under a range of conditions. The set of ignition curves, representing the temperature, pressure and mass fraction behavior of an ignition process, will be transformed to an average generic curve. This average generic curve is the quantitative representation of a combustion modeler's intuitive notion of what is occurring within the combustion process.

The set of parameters needed to morph a specific curve to the generic curve can be also the basis of a parameterization of a given process. For example, there is a distinct and smooth relationship between ignition delay time and ignition starting conditions. This could be used as one of the bases of the parameterization of the curves.

A prerequisite to the production of a generic curve is to establish a new normalized progress parameter in which critical events before ignition are synchronized. This synchronization is necessary because the progress, usually defined by progress time to be the value of one at ignition, is non-linear, i.e. a specific ignition event under differing starting conditions does not occur at the same progress value. In this paper, not just one event is synchronized, such as ignition, is synchronized. Other events, such as the specific definable events on the curve, such as maxima, minima or inflection points, are also synchronized.

An important consequence of this synchronization of chemical events is the ability to compare chemical behavior of the entire range of conditions at each transformed progress point. One such comparison is to take the average behavior at each progress point to form a single generic curve for each species. This single species curve represents the generic behavior of that species over the entire range of conditions. This generic behavior over the range of conditions can provide a generic characterization of the chemical processes involved in ignition. At a given progress value, the relative behavior of each of the individual intermediate species within the process can be compared. The process is basically characterized by one generic curve over progress time for each species.

In this paper, the ethanol mechanism of Marinov (Marinov, 1999), with 50 species, is used. This is a high temperature mechanism and the range of temperatures used in this study are from 1300 to 1400 Kelvin. In addition, this study is limited to lean (0.50) to Stoichiometric (1.0) mixtures.

#### Multiple Synchronizations

In many ignition parameterizations, a single progress variable is used to denote at what stage a process is, from initial conditions, with a value of zero, to the point of ignition, a value of one. In one sense, this can be viewed as normalizing or synchronizing the ignition processes under different starting conditions so that the ignition times line up. The single progress variable indicates the extent of the ignition process.

*Figure 3* shows when the ignition process of times of *Figure 2* are normalized so that the point of ignition, defined by greatest increase of temperature, represent a progress of one. However, the events leading up to

ignition are not completely synchronized. For example, it is evident from the graphs that the maximum points of a given species, signaling a distinct event in the combustion process, do not occur at the same time under different conditions.



Figure 2: Concentration of select species without synchronization.



Figure 3: Synchronization of the curves of Figure 2 to have the ignition time defined at the same progress. In the following sections, a transformation of the time progress will be made to 'actively' line up events within the ignition progress, so, at the end of the transformation, the time progress will represent a distinct phase of the ignition process.

An ignition process goes through distinct phases. During these phases events occur, such as intermediate concentrations reaching a maximum or minimum, leveling off, increasing significantly and other recognizable functional features. These features, along with the time of ignition can also be included in the progress normalization process. In other words, the process time is not just divided by a single factor, the ignition time, but is transformed or morphed in such a way that a set of specified events occur at the same progress value. At the end of this normalization process, not only are the selected events synchronized, but, indirectly, their associated events should also occur at the specific time progress values. The implication is that the progress time is not a steady linear relationship from reactants to ignition, but a nonlinear one where, dependent on the initial conditions, given events deviate from linearity. To facilitate the automatic recognition of events, the ignition events are chosen as distinct features in the curvature of the species behavior, for example, maxima, minima in the values or in their derivatives.

The transformation is based on the intuitive notion that within a given range of conditions the chemical behavior within a process is similar. The human brain recognizes these similarities when examining the species behavior versus time curves of, for example, *Figure 3*. For example, the basic shape of the CH<sub>2</sub>O curves look very similar other than taken a different amount of time to reach its maximum and then fall again. The mathematical transformation of the progress time to ignition through morphing is a quantitative example of the similarity notion.

This paper sets up quantitative mathematical rules so that the similar events under different starting conditions, such as the rise and fall of the CH<sub>2</sub>O mole fractions, are synchronized.

An important consequence of this synchronization of chemical events is the ability to compare chemical behavior of the entire range of conditions at each transformed progress point. One such comparison is to take the average behavior at each progress point to form a single generic curve for each species. This single species curve represents the generic behavior of that species over the entire range of conditions. This generic behavior over the range of conditions can provide a generic characterization of the chemical processes involved in ignition. At a given progress value, the relative behavior of each of the individual intermediate species within the process can be compared. The process is basically characterized by one generic curve over progress time for each species. Figure 4 illustrates that every additional time

synchronization diminishes the spread of the curves, even for a fairly extensive starting condition range. Even within each of the three difference equivalence ratio values, the curves are fairly synchronized.

*Figure 5* shows that when the y-axis is synchronized, i.e. the maximum are all aligned, a single generic curve begins to emerge. This curve represents the general behavior and curvature of the ignition process.



Figure 4: In this figure, both the ignition time and another event, the maximum of H2O2, are synchronized.



Figure 5: The single generic curve over all equivalence ratios emerges as the heights at the maximum are also aligned.



Figure 6:An additional normalization occurs by the defining the maximum to be 1.0



Figure 7: Further alignment with synchronizing the time of  $H_2O_2$ .

Though the synchronization with one extra event synchronizes that species of that event, it can be seen that indirectly, the remaining species, without explicit alignment, are also aligned. *Figure 6* shows the CH<sub>2</sub>O curves with just the ignition aligned. With the extra synchronization of another species, as  $H_2O_2$  shown in Figure 7, nevertheless the CH<sub>2</sub>O curves are brought closer together. Even though the time normalization does not directly involve the CH<sub>2</sub>O species, the spread

of the maxima is diminished with the addition of the normalization due to the H2O2 maxima. This effect is justified by the intuitive notion that the species in a combustion process are acting together, they are not independent of each other.

#### Range of validity and choice of events

A single generic curve is produced by morphing the individual curves to coincide at specified sequential chemical events. This is a mathematical description of the statement that the set of ignition curves have the same mechanistic chemistry. A combustion process undergoing a different set of mechanistic events should be described by a different generic curve. In this formulation 'a different set of mechanistic events' is defined as being a set of curves in which the set of chemical events occur and occur in the same order. This can be used as a criteria for differentiating combustion events with different mechanistic steps. A complete description of a combustion process over the complete set of ranges would be described by a set of generic curves.

This method is general enough to produce a generic curve for a given mechanistic process. The range of validity is in part determined by which chemical events one chooses to use as the basis of morphing. Using fewer chemical events to synchronize the timing of the processes could increase the range of validity, but this could be at the cost of crucial events not being synchronized.

The chemical events to be synchronized is partly a chemical choice. One should choose those events that are crucial to the combustion process. This could either be done through chemical intuition or even through active methods such as, to name one, sensitivity analysis. There is, however, a mathematical criteria. The synchronizing event has to able to be mathematically recognized, for example a maximum, minimum or point of inflection must occur in the combustion process. There is also an additional coverage criteria. The set of synchronizing events should be representative of the different combustion mechanisms that occur within the combustion process (for example the different chemical regimes found by clustering in the paper of (Blurock, 2006, 2004)). In other words, the chosen events should span the entire combustion process being described. Some chemical events can be described by two parameters, for example, both parameters reach a maximum at the same time. Using both parameters would be redundant. In this paper a zero dimensional process over ignition time has been chosen as the example.

But the method itself is purely mathematical and not restricted to only ignition processes. For example, one dimensional flames could be also be described by generic curves. The primary criteria to apply the method described in this paper is that a multivariate event is described by a single variable progress. The example in this paper should be thought of a 'proof of concept', that indeed the synchronization of events does occur and consequences of these synchronizatons can be seen.

#### Synchronizing other progress variables: Enthalpy

The synchronization method described here is not limited to time as a progress variable. For example, a common choice is the standard enthalpy. *Figure 8* shows when the normalized standard enthalpy is used, a fairly good synchronization occurs.

OH Mole Fraction versus Normalized Standard Enthalpy



*Figure 8:* Mole fraction of hydroxyl radical versus normalized standard enthalpy.

However, some improvement can be seen from

*Figure 9* when the progress is morphed so that ignition occurs at progress 0.5. In this figure considerably more alignment can be seen.



Figure 9: Use of normalized standard enthalpy with the additional constraint that ignition occurs at progress 0.5

Using additional synchronization points, as shown in *Figure 10*, even more alignment occurs and the prospect of a better generic curve increases.



Figure 10: The normalized standard enthalpy is synchronized at several points: ignition and the maximums of OH,  $CH_4$  and  $CH_2O$ .

#### **Towards Parameterization**

It is both theoretically and practically important to be able to predict the non-linearity of the time progress and to have a transformation from the generic curve to the actual species curves under varying conditions. Simpler transformations are, of course, better and those that have fewer dependent parameters are also preferable. It is for this reason that perturbations from a generic curve offer a greater opportunity for simpler dependencies, both in the number of parameters needed and in the functional form of the dependence. In addition, with small perturbations from the original curve, errors in the approximation of the perturbation will result in far smaller errors in the original curve. For the ignition progress the perturbation from just ignition normalized time is taken. For the species values, the perturbation from the average or generic curve is taken.

To be able to use the normalized progress with several events, a viable parameterized transformation from the ignition normalized progress is needed. The parameterization will be based on the deviations or perturbations of the ignition normalization. A transformation depends on finding simple relationships between the deviations and known properties (such as temperature, pressure and, possibly a small subset of species concentrations).

*Figure 11* shows the difference between the generic  $H_2O_2$  curve and the actual curves under the different starting conditions. It can be immediately seen that the curves between the synchronized ignition events have a similarity to a second degree polynomial dependence of the normalized progress value. This is substantiated by the *Figure 12* showing this difference between the derived polynomial and the perturbation.

The maximum deviations lie around 10% to 20% and these appear to be most prominent closer to ignition. However, since the perturbations themselves are on the order of 10% to 20%, the maximum absolute errors are

on the order of 1% to 4%. This is an acceptable tolerance for such a simple approximation.

The points leading to ignition have a significantly smaller error. The larger error near ignition is reasonable due to the fact that this is where the greater changes are occurring. These larger errors may be diminished by a higher density of fixed events near ignition.



Figure 11: The difference between the average generic curve and the actual curves under the same starting conditions.



Figure 12: The differences between the piecewise second degree polynomial approximation of the curve differences. The solid lines denote minimum and maximum values and the dotted lines between are the difference values.

For the second degree polynomial, three coefficients are needed. In this example, there are five intervals. Thus, in total fifteen parameters are needed to account for each starting condition difference for each species. However, closer examination of the perturbation curves shows that there can be, as with the ignition progress parameterization, a smooth relationship relative to starting conditions. Thus a simple multi-dimensional function in starting temperature, pressure and equivalence ratio can produce the needed coefficients for each progress interval. Thus the total number of coefficients needed to describe the full set 18 starting conditions used here is expected to be considerably less that than 270 (18, number of conditions, times 15, number of coefficients). For example, if a second degree polynomial dependence could be found for eachcoefficient, where temperature, pressure and equivalence ratio were the independent variables, then seven coefficients would be needed for each coefficient to cover the entire range continuously

#### Timings

For the timing tests, Adiabatic constant volume ignition calculations were made using 6 starting temperatures from 1200 to 1300 degrees Kelvin and 3 equivalence ratios between 0.5 and 1.0 with the ethanol mechanism used throughout this paper. An ignition calculation was made for each starting condition with time step intervals of 10<sup>-5</sup> second intervals until ignition occurred. Timing comparisons were made between a full calculation using the differential solver of Cantera for each time step and two types of tabulated runs. The first tabulated run calculated the full set of mole fractions for all 50 species of the ethanol mechanism from the derived polynomial expressions described previously at each time interval. In this run, for each time interval, the corresponding progress value was calculated and then the species were calculated at that progress. This gives a full oneto-one correspondence to the full calculation. For the second tabulation run, only the corresponding progress value for each ignition time was calculated. For example, for CFD calculations, only the progress variable is 'transported', the specific species values are not needed (only the temperature and pressure are needed in addition). All the calculations were made on a MacBook Pro 5.3 laptop (2.66 GHz Intel Core 2 Duo processor).

Table 1 shows the run times for each individual ignition run for comparison. The speed up factors were calculated simply by taking the ratio of the calculation time of the normal full ignition run and the calculation time of the tabulated runs. It can be seen from this table that there is a large range of run times and speed up factors. These are summarized in Table 1.

#### Conclusions

The intuitive notion that combustion processes within a given range of conditions representing similar mechanistic steps is quantitatively justified with the concept of generic curves over a single parameterization.

The generic curves are produced by synchronizing not only the point of ignition, but a choice of chemical events before ignition. These chemical events can be automatically recognized by distinct mathematical features, such as maxima, minima or inflection points.

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Calculation Mode	Value	Min	Max	Ave
Full	Run(ms)	388	501	453
Tabulated (Species)	Run(ms)	5.54	16.6	15.6
Tabulated (Progress)	(Run(ms)	0.078	0.493	0.0177
Tabulated (Species)	Speedup	25.3	142	67.6
Tabulated (Progress)	Speedup	996	6141	3243

Table 1: This table give a summary of the values from *Table* \*ref{tab:timeperrunandratios} showing the range* of run times that have occurred throughout the different starting run conditions. The first three rows, *with {\bf Run Times}, are the minimum, maximum,* average and total run times for the set of conditions. The next two rows show the minimum, maximum and average speed up ratios (calculated by the ratio of the tabulated time over the full calculation time) for the set of conditions.occurred throughout the different starting run conditions. The first three rows, with {\bf Run *Times}*, are the minimum, maximum, average and total run times for the set of conditions. The next two rows show the minimum, maximum and average speed up ratios (calculated by the ratio of the tabulated time over the full calculation time) for the set of conditions.

# REACTION PATHWAY ANALYSIS OF ReaxFF MD SIMULATIONS WITH VARxMD

Xiaoxia Li<sup>1\*</sup>, Junyi Han<sup>1,2</sup>, Li Guo<sup>1</sup>, Xianjie Qiao<sup>1</sup>, Mo Zheng<sup>1,2</sup>, Xiaolong Liu<sup>1,2</sup> <sup>1</sup> State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, P. R. China 2 University of Chinese Academy of Sciences, Beijing 100049, P. R. China

Keywords: Automated reaction generation, ReaxFF molecular dynamics, visualization, reaction site tracking

ReaxFF is a reactive force field that permits much faster ReaxFF molecular dynamics (ReaxFF MD) simulations than density functional theory (DFT) for large reactive molecular systems. ReaxFF MD is promising in uncovering the complex reaction mechanisms of hydrocarbon fuel combustion and coal pyrolysis<sup>1</sup>. However, the available analysis tools in LAMMPS and ADF lack the ability to catch the species and reaction pathways from the ReaxFF MD simulation trajectory, which are critical in understanding the reaction mechanisms of complex systems.



Figure 1 Snapshot of VARxMD for reaction analysis in a coal pyrolysis system, where bonds to be broken are highlighted in red, and the just formed bonds are in green

This presentation overviews the development and application of VARxMD (Visualization and Analysis of Reactive Molecular Dynamics)<sup>2</sup>, the only code capable of analyzing detailed chemical reactions automatically for ReaxFF MD simulations. VARxMD has exhibited its critical role in revealing the complex reactions in pyrolysis simulation of large scale models of HDPE (7216 atoms), cellulose (7572 atoms), and coal models with up to 28,351 atoms.

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# MECHANISM OF THE OXIDATION OF 1-(FERROCENYL)– ETHANONE/ETHANOL BY DICYANOBIS(PHENANTHROLINE)IRON(III)

Rozina Khattak<sup>\*1,2</sup>, Iftikhar I. Naqvi<sup>1,3</sup>

<sup>1</sup>Department of Chemistry, University of Karachi, Karachi-75270, Pakistan <sup>2</sup>Department of Biochemistry, Shaheed Benazir Bhutto Women University, Peshawar, Pakistan <sup>3</sup>Institute of Environmental Studies, University of Karachi, Karachi-75270, Pakistan

#### Abstract

This study reveals that dicyanobis(phenanthroline)iron(III);  $[Fe^{III}(phen)_2(CN)_2]^+$  oxidizes 1-ferrocenylethanone;  $[CpFe^{II}CpCOMe]$ , and 1-ferrocenylethanol;  $[CpFe^{II}CpCHOHMe]$  through a complex mechanism. The oxidation involves formation of intermediate(s), which takes part in the reaction and gets oxidized. Protonation of the reducing agents yields intermediates that lead the reactions to undergo a complex kinetics in 80% (v/v) aqueous dioxane. A zeroth order triggers the rate of reactions, which follows an overall second order to termination of the reactions, subsequently. The conjugate acid of ferrocenylethanone;  $[CpFe^{II}CpC^+OHMe]$  catalyses the oxidation of  $[CpFe^{II}CpCOMe]$ , the impact of variation in the concentration of protons (0.2 mM – 5.2 mM) showed. An opposite effect highlighted the protonation of ferrocenylethanol to form  $[CpFe^{II}CpCHO^+H_2Me]$  that inhibits the rate of oxidation of  $[CpFe^{II}CpCOMe]$  enhanced by elevation in the ionic strength (primary salt effect), and declined by descending dielectric constant or increasing volume of dioxane, 10 - 50 (% v/v). The results support leading role of  $[CpFe^{II}CpC^+OHMe]$  in the rate-determining step. The neutral  $[CpFe^{II}CpCHOHMe]$  takes part in the rate-determining step of the redox reaction between  $[CpFe^{II}CpCHOHMe]$  and  $[Fe^{II}(phen)_2(CN)_2]^+$ , the observations and neutral results of the influence of ionic strength and dielectric constant substantiate. The outcomes helped to illustrate the depiction of the mechanism for each reaction with proposition of the rate laws.

#### Keywords

Mechanism, Oxidation, Ferrocenylethanone, Ferrocenylethanol, Dicyanobis(phenanthroline)iron(III).

#### Introduction

Ferrocenylethanone and ferrocenylethanol; the organometallic compounds, although remain in focus for long, but their electron transfer reactions with other transition metal complexes are rare, and this subject needs attention. The importance of such studies appear from the report that identifies the antineoplastic activity of ferrocene-containing alcohols (Shago, Swarts, Kreft, & Rensburg, 2007). The activity of an antineoplastic drug remains attributed to the ferrocenium species, which is the ferric (Fe<sup>III</sup>) part of the drug. The redox ac-

Bhutto Women University, Peshawar, Pakistan. E-mail: rznkhattak@yahoo.com

tive enzymes help to oxidise ferrocenyl group, ferrous (Fe<sup>II</sup>) state, of the drug to ferrocenium species, which aids in Chemotherapy (Osella et al., 2000). The mechanism embraces generation of hydroxyl radical (OH<sup>•</sup>) by the interaction of the resulting ferrocenium species with water and oxygen. The DNA strands are cleaved by hydroxyl radical that results in cell death. The one electron-exchange electrochemistry of the ferrocenium/ferrocene containing species is highly appreciated. This reveals important facts corresponding to their activity pattern either in cancer treatment or other procedures, and illustrates the variation profile of the reduction potential of the subject complexes.

Our interest revolves around the mechanistic studies of two redox reactions under similar conditions.

<sup>•</sup> Dr. Rozina Khattak, Assistant Professor, Department of Biochemistry, Shaheed Benazir

Oxidation of (1-ferrocenyl)- ethanone/ethanol by dicyanobis(phenanthroline)iron(III) in aqueous dioxane remains our task. The study aims to follow the reactivity pattern of the two complexes, and to explore the mechanistic pathways.

The literature survey of the reactions of 1-(ferrocenyl)- ethanone/ethanol helped to identify their various derivatives and electrochemical characteristics, but we do not find thorough kinetic studies that highlights the mechanism(s) (Baciocchi, Floris, & Muraglia, 1993; Bechki & Lanez, 2010; Casas et al., 2007; Glidewell, Klar, Lightfoot, Zakaria, & Ferguson, 1996; Jong, Fang, & Lin, 1999; Li, Gayet, Rosselgong, & Haddleto, 2011; Ryabov et al., 1999; Sasaki & Pittman, 1973; Wang & Anzai, 2015; Xu, Nolan, & Cole, 1994). A couple of reports drew our attention, which focused the oxidation of 1-ferrocenylethanone under fixed circumstances. A detailed kinetic description of the oxidation of 1-ferrocenylethanol remains unanswered, yet. The oxidation of 1ferrocenylethanone and 1,1'-diacetylferrocene by ceric sulphate has been studied in sulphuric acid medium (Holeček, Handlíř, & Klikorka, 1979). This study explains the mechanisms reasonably, but it ignores probable formation of various ceric complexes, which may take part in the reactions, as we described in our work (R. Khattak, Naqvi, & Farrukh, 2008). Molecular oxygen was also used to oxidise 1-ferrocenylethanone and formylferrocene in organic solvents, recently (Fomin & Shirokov, 2012). The discussions are comprehensive and the kinetic measurements helped to propose different ways of mechanisms. We extended the margin of contribution in this field, and used a mixed-ligand ferric complex in our study, which plays an important role as a strong oxidizing agent. It's been used in various probes to oxidize a number of compounds of biological importance (Blake, White, & Shute, 1991; Matsumoto et al., 1997; Pelizzetti, Mentasti, & Pramauro, 1978; Takagi, Kagayama, Matsumoto, Tarumi, & Funahashi, 1995). Our interest revolves around a few distinctive properties of this oxidant, such as, its solubility in a mixed aqueousorganic solvent mixture of our interest, high reduction potential, and highly coloured reduced (Fe<sup>II</sup>) species. These characteristics helped us to follow the reaction spectrophotometrically.

#### **Experimental Section**

Analar grade materials were used without further purification, unless otherwise stated. A nitrate salt of dicyanobis(phenanthroline)iron(III) was synthesized, and purified subsequently, as described (Rozina Khattak, 2011; Schilt, 1960). 1-(ferrocenyl)ethanone/ethanol 95-97% were purchased from Acrōs Organics and used without further purification.

The kinetic studies were performed under fixed circumstances of pseudo-first order condition,

and constant pH, ionic strength, dielectric constant, temperature. A change was brought to follow the influence of a parameter retaining all other components constant. Formation of the reduced product, dicyanobis(phen)iron(II);  $[Fe^{II}(phen)_2(CN)_2]$ , was followed spectrophotometrically at 530 nm, to ensue the reaction in 80% (v/v) aqueous dioxane. A rapid kinetic technique was employed during analyses. Application of the integrated rate equations yields kinetic data, and the plots were always linear with R<sup>2</sup> 0.97-1.0. The data are the average of 3-6 readings.

#### **Results and Discussion**

The impact of various factors over the rate of reaction assists to identify the reactive entities and the intermediates. We quantified the effects of variation in the concentration of each reacting entity, and the ionic strength and dielectric constant.

The reactions were observed to undergo different kinetic orders, and as a consequence different zones appeared in the pathways of the reactions. We observed the zeroth order kinetics in the first zone. This is an independent region where any change in the parameters doesn't influence the rate of reactions. An overall second order kinetics leads the rate soon after the first zone finishes. This is the second region, where 1-ferrocenylethanone; [CpFe<sup>II</sup>CpCOMe], or 1ferrocenylethanol, [CpFe<sup>II</sup>CpCHOHMe], and dicyanobis(phen)iron(III); [Fe<sup>III</sup>(phen)<sub>2</sub>(CN)<sub>2</sub>]<sup>+</sup> control the rate of reaction according to the first order, separately. This part of the reaction goes longer until the end of the reaction, but, when the reaction gets closer to cease, we recognized a third zone. In this part, the rate of reaction and the rate of decrease in the solubility of the reduced iron complex,  $[Fe^{II}(phen)_2(CN)_2],$ compete. This zone appears because followed our reaction we spectrophotometrically, and monitored an increase in the absorbance with respect to time considering the high molar extinction coefficient of [Fe<sup>II</sup>(phen)<sub>2</sub>(CN)<sub>2</sub>]. This species is neutral and its solubility is certainly lower than its oxidised form, [Fe<sup>III</sup>(phen)<sub>2</sub>(CN)<sub>2</sub>]<sup>+</sup>, in 80% v/v aqueous dioxane. The concentration of the neutral complex, [Fe<sup>II</sup>(phen)<sub>2</sub>(CN)<sub>2</sub>], reaches at its optimum near the end of the reaction and the third zone observes, consequently.

The increasing concentration of  $[Fe^{III}(phen)_2(CN)_2]^+$  doesn't affect the values of zeroth order rate constant  $(k_{obs})$  as well as the observed pseudo-first order rate constant  $(k'_{obs})$ . This supports the suitability of conditions, we maintained at pseudofirst order. The observed zeroth order rate constant remains unchanged upon increasing the concentration of [CpFe<sup>II</sup>CpCOMe] or [CpFe<sup>II</sup>CpCHOHMe] in the reaction mixture, keeping all other factors constant. No considerable change observed in the multiplication product of  $\varepsilon$  and  $k_{obs}$  ( $\varepsilon k_{obs}$ ). The value of the pseudofirst order rate constant increases, however. An increasing curvature demonstrates the first order dependence of the rate of reaction on [CpFe<sup>II</sup>CpCOMe] or [CpFe<sup>II</sup>CpCHOHMe], when drawn between  $k'_{obs}$  and [CpFe<sup>II</sup>CpCOMe] or [CpFe<sup>II</sup>CpCHOHMe]. The pattern of such increase is different for each case. We recognise this difference in Figure 1 clearly where (*a*) shows the profile of 1-ferrocenylethaone and (*b*) shows it for 1-ferrocenylethanol.



(a). Oxidation of 1-ferrocenylethanone at  $304 \pm 0.5 K$ 



(b). Oxidation of 1-ferrocenylethanol at  $291 \pm 0.5 K$ 

Figure 1. Rate constants as a function of concentration at 0.18 mM (ionic strength, I). The circle and triangle represent the effect of variation in the concentration of  $[Fe^{III}(phen)_2(CN)_2]^+$  over zeroth order data;  $\varepsilon k_{obs}$  ( $\circ$ ), and pseudo-first order rate constant;  $k'_{obs}$  ( $\Delta$ ) when  $[CpFe^{II}CpCOMe]$  is constant, 1.3 mM. The square and dash, show the impact of the concentration of  $[CpFe^{II}CpCOMe]$  or  $[CpFe^{II}CpCHOHMe]$  on the rate constants ( $\varepsilon k_{obs}$ ;  $\Box$ ,  $k'_{obs}$ ; —), respectively, at 0.075 mM  $[Fe^{III}(phen)_2(CN)_2]^+$ . The filled circle ( $\bullet$ ) mentions  $k'_{obs}$ at 1:1 concentration ratio between oxidant and reductant.

The plots of the concentration of  $[CpFe^{II}CpCOMe]$  or  $[Fe^{III}(phen)_2(CN)_2]^+$  as x-ordinates,  $\varepsilon k_{obs}$  and  $k'_{obs}$  as y-ordinates refer to our results (Figure 1, *a*). The curvature stoops at higher concentrations of  $[CpFe^{II}CpCOMe]$ , which is an indication of the formation of probable conjugate acid of 1-ferrocenylethanone;  $[CpFe^{II}CpC^+OHMe]$ . This

intermediate species takes part in the reaction, and provides a reason to bend down the curvature. The oxygen atom of the carbonyl group in acetyl furnishes a site for this protonation. The intercept of the curvature verifies an initial concentration independent rate with respect to [CpFe<sup>II</sup>CpCOMe]. This scenario was further affirmed while a discordant value of  $k'_{obs}$ observed at 1:1 ratio between reductant and oxidant. The value of  $k'_{obs}$  increases linearly upon enhancing the concentration of 1-ferrocenylethanol in the reaction mixture. The reaction follows a first order kinetics with respect to [CpFe<sup>II</sup>CpCHOHMe]. This is the only difference in the behaviour upon increasing the [CpFe<sup>II</sup>CpCOMe] concentration of either or [CpFe<sup>II</sup>CpCHOHMe] in the reaction mixture. The other impacts are all same for each of them.

The oxygen atom of 1-ferrocenylethanol also maintains a site for protonation that yields protonated 1-ferrocenylethanol; [CpFe<sup>II</sup>CpCHO<sup>+</sup>H<sub>2</sub>Me]. To verify protonated the formation of 1-(ferrocenyl)ethanone/ethanol and their participation in the reactions, a set of experiments was performed. A concentration ratio, was fixed 1:10, among [Fe<sup>III</sup>(phen)<sub>2</sub>(CN)<sub>2</sub>]<sup>+</sup> [CpFe<sup>II</sup>CpCOMe] and or [CpFe<sup>II</sup>CpCHOHMe], and the concentration of protons in the reaction mixture was varied. The concentration of protons was always in excess over other reactants. Nitric acid was used as a source of protons. This helps to identify the catalysing impact of protons on  $k'_{obs}$  in case of ferrocenylethanone, and frame the rate decelerating character of protonated ferrocenylethanol. The value of  $\varepsilon k_{obs}$  remains constant as was supposed. A plot of [H<sup>+</sup>] versus  $\varepsilon k_{obs}$  and  $k'_{obs}$  helps to recognise the role of [CpFe<sup>II</sup>CpCOMe] and, or [CpFe<sup>II</sup>CpCHOHMe] as a limiting reactant, because, at higher concentrations of protons the linearity becomes bent (Figure 2; a & b).



(a). Oxidation of 1-ferrocenylethanone at  $306 \pm 0.5 K$ 



(b). Oxidation of 1-ferrocenylethanol at  $291 \pm 0.5 K$ 

Figure 2. The Profile of the effect emerges from increasing concentrations of protons over the rate constants  $(ek_{obs}; \bullet, k'_{obs}; \blacktriangle)$  at 5.1 mM (1), 0.075 mM  $([Fe^{II}(phen)_2(CN)_2]^+)$  and 0.751 mM  $([CpFe^{II}CpCOMe] \text{ or } ([CpFe^{II}CpCHOHMe]).$ 

This pattern also strengthens to explain the bending curvature (Figure 1; *a*) while the concentration of [CpFeIICpCOMe] was in excess over protons and  $[Fe^{III}(phen)_2(CN)_2]^+$ . These results justify formation, and leading role of the conjugate acid of 1ferrocenylethanone; [CpFe<sup>II</sup>CpC<sup>+</sup>OHMe] in the ratedetermining step of the reaction between dicyanobis(phen)iron(III) and 1-ferrocenylethanone. The rate of reaction between dicyanobis(phen)iron(III) and 1-ferrocenylethanol decreases upon protonation of ferrocenylethanol such that the strength of protons retards the rate of reaction. This substantiates 1ferrocenylethanol as an active species that takes part in the rate-determining step of the reaction.

The results were further refined by implementation of the transition state theory. The primary salt effect and the impact of dielectric constant were gauged to distinguish the rate-regulating species. The results were concordant to support our findings (Figure 3-4).



(a). Oxidation of 1-ferrocenylethanone at  $304 \pm 0.5 K$ 



(b). Oxidation of 1-ferrocenylethanol at  $291 \pm 0.5 K$ 

Figure 3. The impact of escalation of ionic strength on  $k'_{obs}$  (secondary x-y coordinates) and  $\varepsilon k_{obs}$  (primary x-y coordinates) at 0.075 mM ( $[Fe^{III}(phen)_2(CN)_2]^+$ ) and 0.751 mM ( $[CpFe^{II}CpCOMe]$  or  $[CpFe^{II}CpCHOHMe]$ ).



(a). Oxidation of 1-ferrocenylethanone at  $304 \pm 0.5 K$ 



(b). Oxidation of 1-ferrocenylethanol at 291  $\pm$  0.5 K

Figure 4. Effect of increasing proportion of dioxane in the reaction mixture, on  $k'_{obs}$  ( $\blacktriangle$ ) and  $\varepsilon k_{obs}$  ( $\bullet$ ). The experimental conditions were affixed at 0.075 mM ([Fe<sup>III</sup>(phen)<sub>2</sub>(CN)<sub>2</sub>]<sup>+</sup>), 0.751 mM ([CpFe<sup>II</sup>CpCOMe] or [CpFe<sup>II</sup>CpCHOHMe]) and a zero ionic strength.

#### Proposed Mechanism(s)

The results in the view of literature, help to propose following mechanisms of the redox reactions between [Fe<sup>III</sup>(phen)<sub>2</sub>(CN)<sub>2</sub>]<sup>+</sup> and [CpFe<sup>II</sup>CpCOMe], or, [Fe<sup>III</sup>(phen)<sub>2</sub>(CN)<sub>2</sub>]<sup>+</sup> and [CpFe<sup>II</sup>CpCHOHMe]. An of initial protonation [CpFe<sup>II</sup>CpCOMe] or to [CpFe<sup>II</sup>CpCHOHMe] form conjugate acid establishes the equilibrium between [CpFe<sup>II</sup>CpCOMe] and [CpFe<sup>II</sup>CpC<sup>+</sup>OHMe], and or, [CpFe<sup>II</sup>CpCHOHMe] and [CpFe<sup>II</sup>CpCHO<sup>+</sup>H<sub>2</sub>Me]. Both of the species, unprotonated and protonated, take part to donate electron to [Fe<sup>III</sup>(phen)<sub>2</sub>(CN)<sub>2</sub>]<sup>+</sup> and undergo a zeroth and an overall second order kinetics. The rateor slow step depends upon the determining [Fe<sup>ÎII</sup>(phen)<sub>2</sub>(CN)<sub>2</sub>]<sup>+</sup> concentration of and [CpFe<sup>II</sup>CpC<sup>+</sup>OHMe] in the reaction mixture, and [Fe<sup>III</sup>(phen)<sub>2</sub>(CN)<sub>2</sub>]<sup>+</sup> and [CpFe<sup>II</sup>CpCHOHMe], during oxidation of 1-ferrocenylethone and 1-ferrcenylethanol, unprotonated respectively. The species. [CpFe<sup>II</sup>CpCOMe], and the protonated species; [CpFe<sup>II</sup>CpCHO<sup>+</sup>H<sub>2</sub>Me] withdraw electron to [Fe<sup>III</sup>(phen)<sub>2</sub>(CN)<sub>2</sub>]<sup>+</sup> through an overall zeroth order kinetics in each reaction, respectively. The mechanism for each reaction is proposed separately that yields rate law(s) as follows:

Oxidation of 1-Ferrocenylethanone by Dicyanobis(phen)iron(III)



Oxidation of 1-Ferrocenylethanol by Dicyanobis(phen)iron(III)



R = Methyl group

$$\begin{bmatrix} Fe^{III} (phen)_{2} (CN)_{2} \end{bmatrix}^{+} + \begin{bmatrix} CpFe^{II} CpCHO^{+}H_{2}Me \end{bmatrix} \xrightarrow{k_{1}(fast)} \\ Fe^{II} (phen)_{2} (CN)_{2} \end{bmatrix} + \begin{bmatrix} CpFe^{III} CpCHOHMe \end{bmatrix}^{+} + \begin{bmatrix} H \end{bmatrix}^{+} \\ \begin{bmatrix} Fe^{III} (phen)_{2} (CN)_{2} \end{bmatrix}^{+} + \begin{bmatrix} CpFe^{II} CpCHOHMe \end{bmatrix} \xrightarrow{k_{2}(slow)} \\ \begin{bmatrix} Fe^{II} (phen)_{2} (CN)_{2} \end{bmatrix}^{+} + \begin{bmatrix} CpFe^{III} CpCHOHMe \end{bmatrix}^{+} \\ Rate = k_{1} \begin{bmatrix} CpFe^{II} CpCHO^{+}H_{2}Me \end{bmatrix}^{0} \begin{bmatrix} Fe^{III} (phen)_{2} (CN)_{2}^{+} \end{bmatrix}^{0} + \\ k_{2} \begin{bmatrix} CpFe^{II} CpCHOHMe \end{bmatrix}_{T} \begin{bmatrix} Fe^{III} (phen)_{2} (CN)_{2}^{+} \end{bmatrix} \\ (1 + K_{eq} \begin{bmatrix} H^{+} \end{bmatrix}) \end{bmatrix}$$

#### Conclusions

The study elucidates formation of protonated 1-(ferrocenyl)- ethanone/ethanol in aqueous dioxane. These potonated species lead the mechanism of the reactions. The protonated 1-ferrocenylethaone takes part in the rate-determining or the slow-step, and the unprotonated 1-ferrocenylethaone however, involves preceding the reaction under zeroth order kinetics. A reverse pattern observes for 1-ferrocenvlethanol. The equilibrium between the unprotonated and protonated species, suggests the rate of electron transfer, and the mechanistic routes. Dicyanobis(phen)iron(III) takes an electron without forming any intermediate species such as it doesn't protonate. The values of the electrode potential ( $E_{1/2}$ ) and the self-exchange rate constant ( $k_{22}$ ) of protonated ferrocenyletnaone, [CpFe<sup>II</sup>CpC<sup>+</sup>OHMe], were calculated by employing the relationship of Gibbs free energy with the equilibrium constant and the cell potential, and the Marcus cross-relation. The literature cited values of  $E_{1/2}$  and self-exchange rate constants to dicyanobis(phen)iron(III/II) couple  $([Fe^{III/II}(phen)_2(CN)_2]^{+/0})$ , 2-ferrocenylethanol couple ([CpFe<sup>III/II</sup>CpCH<sub>2</sub>CH<sub>2</sub>OH]<sup>+/0</sup>) and 1-ferrocenylethanol couple ([CpFe<sup>III/II</sup>CpCHOHMe]<sup>+/0</sup>) helped to evaluate the approximations to the conjugate acid of 1ferrocenylethanone ([CpFe<sup>III/II</sup>CpC<sup>+</sup>OHMe]<sup>+/0</sup>).(Castillo, 1986; Garcia,

Karlin, & Holwerda, 1987; Matsumoto et al., 1997; Ryabov et al., 1999; Takagi et al., 1995; Wynn, Knaff, & Holwerda, 1984) The approximations,  $E_{1/2}$  and  $k_{22}$ , were estimated to be 0.204 V and 5.7 × 10<sup>4</sup> M<sup>-1</sup> s<sup>-1</sup>, respectively. This is worthwhile to consider the structural difference among 1-ferrocenylethanol, 2ferrocenylethanol, 1and protonated ferrocenylethanone. The former two metallocenes are the isomers although, but their properties to exchange electrons are very much different owing to the position of the hydroxyl group. This brings a large difference between the redox potential and the self-exchange rate constants therefore. The hydroxyl group in 2ferrocenylethanol doesn't strongly withdraw electrons than in 1-ferrocenylethanol. The figure of the reduction potential is higher for the former than the latter one, conjugate consequently. The acid of 1ferrocenylethanone is somehow identical to 1ferrocenylethanol, but, the two metallocenes should be different in properties. 1-ferrocenylethanol is saturated at carbon attached to oxygen, and stable. The conjugate acid is, however unsaturated at carbon attached to oxygen that must lead to form a carbonium ion, which is itself reactive and energetic. Such conduct of ratecontrolling properties of protonated ferroceylethanone was strengthened, while the ratedetermining step involved 1-ferrocenylethanol in the oxidation of 1-ferrocenylethanol by dicyanobis(phen)iron(III). This leads to the conclusion that the oxidation of either of 1-ferrocenylethanone or 1-ferrocenylethanol is constrained by the protonated carbonyl group either unsaturated at carbon centre; [CpFe<sup>II</sup>CpC<sup>+</sup>OHMe] or, saturated; [CpFe<sup>II</sup>CpCHOHMe]. The values of the pseudo-first with order rate constant respect to 1ferrocenylethanone or 1-ferrocenylethanol remain almost same, and equivalent. This study reveals an important feature of these two reactants; 1ferrocenylethanone and 1-ferrocenylethanol, that, the protonation of the carbonyl group is an important factor in the oxidation of the derivatives of ferrocene, though restraining its properties either chemical activity or biological effects.

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# QUENCHING PROCESSES UNDER RESTRICTED GEOMETRY CONDITIONS: A QUANTITATIVE TREATMENT

M. Marchena, F. Sánchez Burgos, E, Bernal, A. Barrios, J. A. Lebrón, B. Sarrión,
 P. López-Cornejo, C. Carmona, M. L. Moyá and M. López-López<sup>\*†</sup>
 University of Seville – Seville and <sup>†</sup>University of Huelva-Huelva

#### Abstract

Chemical reactivity under restricted geometry conditions can be described through the equations of the Pseudophase Model (a two state model). This model is based on the assumption of an equilibrium between these two states (free and bound) which is not perturbed by the reactive event. This implies that the reaction in which these states participate must be slow, in relation to the exchange processes between the two states. This condition holds in the case of chemical reactions, but does not hold for very rapid photochemical reactions. However, the Pseudophase Model seems to be applicable, *apparently*, in the case of excited state reactions. In this case the meaning of the parameters appearing in the equations is different from that corresponding to ground state reactions.

To clarify this point, the quenching of the fluorescence emission of 1-pyrene-carboxaldehyde by the iodide ion has been studied in the presence of several receptors (DNA, micelles, and cyclodextrins). The reactivity can be *formally* rationalized using the Pseudophase Model. The quantitative analysis of the parameters has been carried out employing a formulation previously developed by us.

#### Keywords

Restricted geometry conditions, Pseudophase Model, quenching processes.

#### Introduction

In solution some chemical species (ligands) have the tendency to accumulate at the surface (or inside) of receptors such as micelles, polymers, cyclodextrins, etc. This fact arises from favorable binding free energies, as a consequence of the interaction between the receptor and the ligand. Therefore, a change in the chemical potential of the ligand (and the receptor), as measured through their activity coefficients, is observed. It can easily be shown that for a species, S, that interacts with a receptor, M, the activity coefficient and the chemical potential of S is given by (Gomez-Herrera et al., 2004):

$$\gamma_{\rm S} = \frac{1}{1 + K [M]} \qquad (a)$$

$$\Delta \mu_{\rm S} = RT \ln \gamma_{\rm S} \qquad (b)$$

In this equation K is the equilibrium constant corresponding to the process

$$S_F + M \stackrel{K}{\rightleftharpoons} S_B$$
 (2)

Here  $S_F$  and  $S_B$  represent the free and bound (to the receptor) states of S, respectively. If S participates in a chemical reaction, the process occurs *under restricted geometry conditions*. When the receptor concentration varies, the reaction rate will change because of the variations in the S free energy. These changes are described by the so Pseudophase Model (Menger and Portnoy, 1967). According to this model, *if*  $S_F$  *is in* 

*equilibrium with*  $S_B$ , the observed rate constant, for a unimolecular ground state process, is given by:

$$k_{obs} = \frac{k_F + k_B K[M]}{1 + K[M]}$$
(3)

 $k_{\rm F}$  and  $k_{\rm B}$  being the rate constant corresponding to the reactions of  $S_{\rm F}$  and  $S_{\rm B}$ , respectively. As was previously reported (Gomez Herrera et al., 2004 and Lopez-Cornejo et al., 2002), the Pseudophase Model is flexible enough to extend to other more complicated cases. Notice that differences in the reactivity of  $S_{\rm F}$  and  $S_{\rm B}$  arise from chemical and physical factors.

This work deals with the application of the Pseudophase Model to excited state processes. An intriguing fact observed in relation to the quenching processes occurring under restricted geometry conditions is that equation 3 seems to describe adequately the variations in the reaction upon changing [M], in spite of the fact that the equilibrium condition between free and bound reactants does not hold (Lopez-Cornejo and Sanchez, 2001). This situation was considered from a theoretical point of view and an original treatment was developed in a previous paper (Marchena and Sanchez, 2010 and Sanchez et al., 2014). This treatment is checked for the quenching process of pyrene-1- carboxaldehyde by iodide ion in presence of polyelectrolytes (DNA), cyclodextrins and micellar solutions as receptors.

To whom all correspondence should be addressed (manuel.lopez@diq.uhu.es)

#### **Experimental section**

The quenching process of pyrene-1carboxaldehyde (pyCHO) by iodide ions was studied by steady-state fluorescence. The receptors were Calf Thymus DNA, micellar solutions of cetyltrimethylammonium chloride (cationic), CTAC, and sodium dodecylsulfate (anionic), SDS, and mixtures of  $\beta$ - and 2-hydroxypropyl- $\beta$ - cyclodextrins ( $\beta$ -CD and  $\beta$ -HCD and. The total ionic strength was fixed at 0.1 mol dm<sup>-3</sup>.

#### **Results and Discussion**

#### Interaction of a ligand with a single receptor

The fluorescence quenching process of pyCHO by I in aqueous solutions of DNA has been studied. PyCHO binding to DNA can be characterized from ligand emission intensity measurements because of the different emission showed by the free and bound (to the polynucleotide) states.

$$PyCHO + ADN \xleftarrow{K} PyCHO / ADN \qquad (4)$$

As is seen the intensity decreases with increasing DNA concentration (Figure 1A). This behavior proceeds from the existence of two excited states of PyCHO with next energy, a non-emissive dark state and an emissive state. The relative population of these two states depends on the dielectric constant of the PyCHO environment, the dark state being favored by a decrease in the dielectric constant of the medium. These changes can be described by the equation:

$$I = \frac{I_f + I_b K[M]}{1 + K[M]}$$
(5)

In this equation K represents the (true) binding constant of pyCHO to DNA.  $I_f$  and  $I_b$  are the emission intensities of free and bound pyCHO to the polyelectrolyte, respectively. From the fitting of the experimental data by using eq. 5, the binding constant of pyCHO to DNA obtained was 9400 mol<sup>-1</sup> dm<sup>3</sup>.

The emission intensities of pyCHO at different concentrations of quencher and receptor were also determined to obtain the Stern-Volmer constants.

$$\frac{I_0}{I} = 1 + (K_{SV})_{obs}[I^-]$$
(6)

Results showed a linear Stern-Volmer plot in the absence of DNA. However, in the presence of the polynucleotide no linear behavior was observed. This would point out that the observed Stern-Volmer constant,  $(K_{SV})_{obs}$ , with respect to the concentration of quencher. was observed In this cases,  $(K_{SV})_{obs}$ , depends on the quencher concentration, [I<sup>-</sup>]. With this in mind  $(K_{SV})_{obs}$  was determined for each [I<sup>-</sup>]. The Stern-Volmer constants obtained for [I<sup>-</sup>]= 0.08 mol dm<sup>-3</sup> are plotted *vs* [DNA] in Figure 1B. It is interesting to note that the data in the figure can be fitted by using eq. 7

(see Marchena and Sanchez, 2010 and Sanchez et al., 2014):

$$(K_{SV})_{obs} = \frac{(K_{SV})_{f} + (K_{SV})_{b} K_{app}[M]}{1 + K_{app}[M]}$$
(7)

where  $K_{app}$  is the equilibrium binding constant of the pyCHO to DNA.  $(K_{SV})_b$  and  $(K_{SV})_f$  are the Stern-Volmer constants when fluorophore is bound and free, respectively.  $K_{app}$  values obtained for the different quencher concentrations are listed in Table 1 as  $(K_{app})_{exp}$ . One can see that  $K_{app}$  depends on quencher concentration, and are different from the value of K obtained from emission intensities. Consequently, they are not true binding constants but apparent binding constants. It can be shown, in fact, that these apparent binding constants are given by (Marchena and Sanchez, 2010 and Sanchez et al., 2014):

$$K_{app} = K \frac{a_b}{a_f} = K \frac{\phi_b}{\phi_f} \frac{\varepsilon_b}{\varepsilon_f}$$
(8)

In this equation  $\phi_i$  (i= f, b) are the quantum yields of the free and bound species and  $\epsilon_i$  the corresponding molar extinction coefficients. It can be easily shown that  $a_b/a_f = I_b/I_f$ .



Figure 1. (A) Emission intensity of pyCHO in aqueous solutions of different [DNA]. (K<sub>SV</sub>)<sub>obs</sub>, for the quenching of pyCHO by I as a function of the receptor concentrations in: (B) DNA ([I<sup>-</sup>] = 0.08 mol dm<sup>-3</sup>), (C) CTAC micelles ([I<sup>-</sup>] = 0.1 mol dm<sup>-3</sup>) and (D)equimolecular mixtures of CD ([I<sup>-</sup>] = 0.1 mol dm<sup>-3</sup>).

 $I_b/I_f$  values are summarized in Table 1 for each quencher concentration. It is important to note that  $I_f$  are experimental values but  $I_b$  were obtained from the fit of the emission intensities, when the solution contained the quencher, to equation 5. Solubility problems precluded the experiments at enough high DNA concentration to reach the complete binding of pyCHO to the receptor.

Table 1. I<sub>b</sub>/I<sub>f</sub> and K<sub>app</sub> values corresponding to the photochemical reaction between pyCHO and I in DNA solutions at different concentrations of I.

10 <sup>2</sup> [I <sup>-</sup> ]/ mol dm <sup>-3</sup>	(K <sub>app</sub> ) <sub>exp</sub> / mol <sup>-1</sup> dm <sup>3</sup>	$I_b/I_f$	(K <sub>app</sub> ) <sub>calc</sub> / mol <sup>-1</sup> dm <sup>3</sup>
2	700±198	0.08	752±112
4	1200±216	0.11	1019±182
6	1400±213	0.13	1222±182
8	1800±164	0.18	1692±252
10	2200±281	0.22	$2068 \pm 308$

 $I_b/I_f\,$  values in Table 1 are dependent on the quencher concentration. This would result in curved Stern-Volmer plots for a given DNA concentration, as was experimentally observed.  $(K_{app})_{calc}$  values listed in Table 1 were obtained by using eq. 8. It is worth noting that  $(K_{app})_{calc}$  and  $(K_{app})_{exp}$  are in reasonable good agreement.

# Interaction of a ligand with a mixture of receptors (micelles and monomers)

The quenching process of pyCHO by I<sup>-</sup> was investigated in micellar solutions of CTAC and SDS. PyCHO can interact with two types of receptors: monomers and micelles. In the presence of SDS, the fluorophore accumulates at the micellar interface, whereas the quencher is repelled from the aggregates. Consequently, a diminution in  $(K_{SV})_{obs}$  is observed when the micelles concentration increases. The experimental data can be fitted by using eqs. 5 and 7. However, I<sub>f</sub>, K and  $(K_{SV})_{f}$  have a different meaning (Sanchez et al., 2014). It was shown that:

$$K = \frac{K'_{M}}{1 + K'_{m}[cmc]} \qquad I_{f} = \frac{I_{s} + I_{m}K'_{m}[cmc]}{1 + K'_{m}[cmc]}$$
$$(K_{SV})_{f} = \frac{(K_{SV})_{s} + (K_{SV})_{m}\frac{I_{m}}{I_{s}}K'_{m}[cmc]}{1 + \frac{I_{m}}{I_{s}}K'_{m}[cmc]} \qquad (9)$$

where  $K_m$  and  $K_M$  are the (true) binding constants of the fluorophore to monomers (m) and micelles (M), respectively, and  $I_m$  and  $I_M$  are the corresponding emission intensities.  $I_s$  is the emission intensity of the free fluorophore, that is, in the solvent. ( $K_{SV}$ )<sub>s</sub> and ( $K_{SV}$ )<sub>m</sub> are the Stern-Volmer constants when pyCHO is free and bound to the monomers, respectively.

In the CTAC, both pyCHO and I<sup>-</sup> accumulate at the micellar interface, so that a maximum in the quenching is observed (see Figure 1C). For all CTAC concentrations linear Stern-Volmer plots were observed. According to this, the values of the experimental Stern-Volmer constants,  $(K_{SV})_{obs}$ , are given by (Sanchez et al., 2014):

$$(K_{SV})_{obs} = \frac{(K_{SV})_{f} + (K_{SV})_{b}K_{Q}K_{app}[M]}{1 + [K_{Q} + K_{app}][M] + K_{Q}K_{app}[M]^{2}}$$
(10)

In this equation  $K_Q$  is the (true) binding constant of the quencher to the CTAC micelles and  $K_{app}$  is the binding constant of the pyCHO to the micelles.  $(K_{SV})_b$  and  $(K_{SV})_f$  are the Stern-Volmer constants for the bound (to the micelles) and free (at the cmc) pyCHO. The meaning of  $(K_{SV})_f$  is the same than in the case of SDS micelles. By fitting  $(K_{SV})_{obs}$  to eq. 10, the values of the binding constants were  $164\pm31$  and  $3500\pm976$  mol<sup>-1</sup> dm<sup>3</sup>.

The binding constants of pyCHO and I to CTAC micelles were determined from fluorescence intensities applying eq. 5 and following the procedure of Sarpal and Dogra (Sarpal and Dogra, 1995), respectively. K=  $19000\pm1076 \text{ mol}^{-1} \text{ dm}^3$  and K<sub>Q</sub>=  $175 \text{ mol}^{-1} \text{ dm}^3$  were obtained. The latter value close to  $164\pm31 \text{ mol}^{-1} \text{ dm}^3$ , which was estimated from the fitting of (K<sub>SV</sub>)<sub>obs</sub> to eq. 10.

However,  $K_{app}$ = 3500±976 mol<sup>-1</sup> dm<sup>3</sup> (Figure 1C) differs from the value of the (true) binding constant of pyCHO obtained from intensity data, K= 19000±1076 mol<sup>-1</sup> dm<sup>3</sup>. This difference could be explained by considering eq. 8. In this case,  $a_b/a_f$  depends on micellar and quencher concentration (Sanchez et al., 2014).

$$\frac{a_{b}}{a_{f}} = \frac{\frac{(k_{r})_{b}}{(k_{r})_{b} + (k_{nr})_{b} + (k_{q})_{b}} \frac{K_{Q}[Q]}{1 + K_{Q}[M]}}{\frac{(k_{r})_{f}}{(k_{r})_{f} + (k_{nr})_{f} + (k_{q})_{f}} \frac{[Q]}{1 + K_{Q}[M]}} \epsilon_{f}}$$
(11)

Here the rate constants have the usual meaning. The values of  $a_b/a_f$  were obtained by using eq. 11. The rate constants were determined from quantum yields measurements and fluorescence lifetimes. These values oscillate from 0.188 to 0.222. As can be seen,  $a_b/a_f$  is practically constant, with an average value of 0.205. This result justifies that in the present case linear Stern-Volmer plots were obtained for the whole range of quencher concentration. Eq. 11 renders a  $K_{app}$  value of 3900±221 mol<sup>-1</sup> dm<sup>3</sup>, which is in good agreement with that obtained from the fitting of ( $K_{SV}$ )<sub>obs</sub> by using eq. 10,  $K_{app}$ = 3500±976 mol<sup>-1</sup> dm<sup>3</sup>. This result gives strong support to our treatment.

# Interaction of a ligand with a mixture of two (or more) receptors (cyclodextrins)

The quenching of pyCHO by iodide ion in mixtures of  $\beta$ - and 2-hydroxypropyl- $\beta$ - cyclodextrins ( $\beta$ -CD and  $\beta$ -HCD) was investigated in order to check the new model. Although several classes of mixtures were studied, here we will only refer to the results obtained in a mixture that is a model of a receptor containing two kinds of binding sites with different affinities towards a ligand. This class of mixtures was prepared mixing equimolecular amounts of both CDs.

In the presence of CDs, the fluorophore inserts into the CD cavity and a diminution of the emission intensity of pyCHO as well as in  $(K_{SV})_{obs}$  was observed

when the total concentration of CD in the mixture increases (see Figure 1D). These results are similar to those obtained in the case of a single receptor and the experimental data can be fitted by using eqs. 5 and 7. However, K,  $I_b$ ,  $K_{app}$  and  $(K_{SV})_f$  have a different meaning (Bernal et al, 2014). One can write:

$$K = K_{1} + K_{2} \qquad I_{b} = \frac{I_{1}K_{1} + I_{2}K_{2}}{K}$$

$$K_{app} = K_{app1} + K_{app2} \qquad (10)$$

$$(K_{SV})_{b} = \frac{(K_{SV})_{1}K_{app1} + (K_{SV})_{2}K_{app2}}{K_{app1} + K_{app2}}$$

where  $K_i$  (i= 1 ( $\beta$ -CD), 2 ( $\beta$ -HCD)) is the binding constant of pyCHO to the receptor i, Ii is the emission intensity at a concentration of receptor high enough to cause complete binding of the fluorophore to the receptor in absence of quencher, K<sub>app i</sub> is the apparent binding constant of pyCHO to the receptor and (K<sub>SV</sub>)<sub>i</sub> is the Stern-Volmer constant when the fluorophore is bound to the receptor. Each one of these parameters have been determined in solutions containing one of the receptors:  $K_1 = 835 \text{ mol}^{-1} \text{ dm}^3$ ,  $K_2 = 1550 \text{ mol}^{-1} \text{ dm}^3$ ,  $I_1=0.688$ ,  $I_2=$  0.677,  $K_{app 1}=$  5010 mol<sup>-1</sup> dm<sup>3</sup>,  $K_{app 2}=$ 3100 mol<sup>-1</sup> dm<sup>3</sup>,  $(K_{SV})_1 \approx 0$  mol<sup>-1</sup> dm<sup>3</sup> and  $(K_{SV})_2 = 16$ mol<sup>-1</sup> dm<sup>3</sup> (([I<sup>-</sup>]= 0.1 mol dm<sup>-3</sup>). With this data and eq. 10 the values of K,  $I_b$ ,  $K_{app}$  and  $(K_{SV})_b$  can be calculated and they can be compared to those obtained from the fitting of pyCHO fluorescence intensity in absence of quencher and that of  $(K_{SV})_{obs}$  (Figure 1D) by using eqs. 5 and 7, respectively, (see Table 2). A good agreement was found for the two sets of data.

#### Table 2. Values of K, $I_b$ , $K_{app}$ and $(K_{SV})_b$ corresponding to the quenching process pyCHO and I in equimolecular mixtures of CDs ([I]= 0.1 mol dm<sup>-3</sup>).

	Experimental (fit to eq. 5 and 7)	Calculated
K/mol <sup>-1</sup> dm <sup>3</sup>	2100	2400
$I_{b}/u.a.$	0.682	0.681
$K_{app}/mol^{-1} dm^3$	7400	8100
$(K_{SV})_b/mol^{-1} dm^3$	4.6	6.1

#### Conclusions

In this work, a treatment previously developed by some of us was used for quantitatively rationalizing the experimental data obtained for the quenching of pyCHO by iodide ions in the presence of several receptors have been quantitatively explained. The experimental observations that the binding constants of the fluorophore to the receptors were different depending on the procedure employed in their determination were also explained.

The treatment proposed by the authors accounts for the reason of the Pseudophase Model *formal* applicability to photochemical reactions under restricted geometry conditions.

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# PECULIARITIES OF THE REACTIONS BETWEEN EARLY LANTHANIDE(III) IONS AND AN ANIONIC PORPHYRIN

Zsolt Valicsek\*, Melitta Patrícia Kiss, Muhammad Imran and Ottó Horváth Department of General and Inorganic Chemistry, Institute of Chemistry, Faculty of Engineering, University of Pannonia Egyetem str. 10., Veszprém, H-8200, Hungary

#### Abstract

Insertion of early lanthanide(III) ions into the coordination cavity of porphyrins is a slow and complicated process in aqueous solution, originating from the stability of their aqua complexes and their possible oligomerization. The presence of potential axial ligands can accelerate the coordination of the first porphyrin, but it can hinder the connection of a further porphyrin. Lanthanide ions may coordinate not only to the pyrrolic nitrogens of porphyrins but, under kinetic control, also to the peripheral substituents possessing O-donor atoms. In the case of such anionic porphyrins, the coordination position of metal ions can be influenced by the change of temperature.

#### Keywords

simultaneous metal and ligand control, out-of-plane metalloporphyrins, early lanthanide(III) ions, tail-to-tail oligomerization.

#### Introduction

Porphyrins are peculiar ligands in the respect of complexation because, due to their planar, cyclic, rigid, aromatic, tetradentate, as well as protonated structure, the formation of metalloporphyrins is a special ligand-controlled reaction. As a consequence of the coordination cavity's limited size, the metal ions, depending on their radius, can occupy an in-plane (IP) or an out-of-plane (OOP or SAT=sitting-atop) position. Due to the out-of-plane position, a larger metal ion can simultaneously coordinate to two macrocycles, and, reversely, two metal ions can connect to one ligand, resulting in the formation of so-called sandwich complexes with various compositions (Horváth et al., 2012). Lanthanide(III) ions offer good opportunities for the fine tuning of the out-of-plane distances of the metal center, utilizing the well-known lanthanide contraction. Nevertheless, they incline to higher coordination number (8-12), therefore the investigation of their monoporphyrins is complicated: another multidentate, but O-donor ligand must be applied to hinder the coordination of the second porphyrin to the metal ion (Valicsek et al., 2012).

#### Results

In this work, we studied the reaction between the anionic 5,10,15,20-tetrakis(4-sulfonatophenyl) porphyrin and early lanthanide(III) ions (Ln = La, Ce, Nd, Sm) under various conditions.

\* Corresponding author:

valicsek@vegic.uni-pannon.hu

Lanthanide(III) ions are hard Lewis acids, due to the classification of Pearson, therefore, their insertion into the coordination cavity of the tetradentate, N-donor porphyrin ligand is a slow and complicated process in aqueous solution, originating partly from the strong bond of the solvent molecules to the metal ions. The other reason for the simultaneous metal control in these typical ligand-controlled reactions is that the lanthanide ions may compose oligomer forms through the counter-anion or hydroxide bridges in aqueous solution, the pre-dissociation step of which is required for the formation of porphyrin complexes, too (Fig. 1, Kiss et al., 2014).



Figure 1. Decrease of the apparent formation rate constant of samarium(III)-monoporphyrin with the increase of initial Sm<sup>3+</sup> concentration. (Calculated data from the assumption of tetramers.)

From the study of the reaction rate of porphyrin's metalation at different concentration of lanthanide(III) ions, we are able to indirectly estimate the degree of this oligomerization, as well as the stability constants of these oligomers, the determination of which is very complicated even with special analytical techniques.

# $$\begin{split} &H_2 P^{4-} + (Ln^{3+})_s \Leftrightarrow Ln^{III} P^{3-} + (Ln^{3+})_{s-1} + 2H^+ \\ &k_+^{\prime(oligomer)} = \Phi_1^{oligomer} (Ln^{3+}) \times k_+ ((Ln^{3+})_1) \end{split}$$

As a further consequence of the Pearson-type hard character of lanthanide(III) ions, they can coordinate rather to the peripheral substituent of porphyrin (e.g. to the ionic group ensuring watersolubility), if it possesses similarly hard O-donor atom (e.g. carboxy-phenyl), than to the pyrrolic nitrogens. However, this phenomenon was previously unknown for the sulfonato-phenyl porphyrin (Fig. 2). At lower temperatures (and in the absence of acetate), the position of the free-base porphyrin's UV-Vis absorption bands did not change; only their intensities were approximately dimidiated. Under this kinetic control, the early lanthanide(III) ions were not able to coordinate into the cavity, rather to the sulfonato groups; resulting in the formation of the free-base ligands' tail-to-tail oligomer. Only under thermodynamic control, i.e. at higher temperatures, can coordinate the metal ion also, or rather, to the four pyrrolic nitrogens; resulting in the formation of typical metalloporphyrin complexes (Fig. 3, Kiss et al., 2014).



Figure 2. Structure of the anionic porphyrin's tail-totail dimer, connected by a lanthanide(III) ion.



Figure 3. Temperature dependence (using Eyring-Polányi equation) of the rate constant.

After the discovery of the possible coordination bonds between lanthanide ions and sulfonato substituents, the formation of lanthanide bisporphyrins, in the absence of acetate, may be imagined as a tail-to-tail dimerization of two metallomonoporphyrin complexes through a metal bridge,

similarly to the free-base porphyrins (Fig. 2), and deviating from the head-to-head connection as in the case of sandwich complexes. This assumption may be confirmed by the large similarities between the UV-Vis absorption spectra, as well as the singlet-1 fluorescence spectra of these early lanthanide(III)-mono- and bisporphyrin complexes. These spectral similarities and comparable fluorescence quantum yields may only originate from very weak  $\pi$ - $\pi$  interactions between the macrocycles. If these interactions may be stronger, the absorption bands should show much larger redshifts and hyperchromicities, and the fluorescence should be much weaker, nearly disappear. This was manifested in the case of the (parallel) head-to-tail dimer of the protonated porphyrin, (H<sub>4</sub>TSPP<sup>2-</sup>)<sub>2</sub>, and of the bisporphyrins of mercury(II) ion: (parallel) head-to-tail Hg<sup>II</sup><sub>2</sub>(TSPP)<sub>2</sub><sup>8-</sup> and typical head-to-head Hg<sup>II</sup><sub>3</sub>(TSPP)<sub>2</sub><sup>6-</sup> (Valicsek et al., 2013). However, other special types of aggregation (e.g. perpendicular head-to-tail) among lanthanide-monoporphyrins may occur, too, chiefly at higher porphyrin concentration.

#### Conclusions

As a conclusion, we can declare that the coordination ability and the concentration of the counter-anion of lanthanide ions, as well as the temperature have significant effects on the formation of metalloporphyrins, on their composition, as well as on their oligomerization.

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# OXIDATION OF PYRUVIC ACID AND LACTIC ACID INDUCED BY OH RADICALS IN AQUEOUS SOLUTION

Thomas Schaefer<sup>\*</sup> and Hartmut Herrmann Leibniz Institute for Tropospheric Research – Leipzig Permoserstraße 15 04318 Leipzig, Germany

#### Abstract

The tropospheric oxidation of volatile and semivolatile organic compounds (VOCs) can be induced by radical reactions, which can occur in the gas phase and in the liquid phase (cloud droplets, fog, rain or hygroscopic particles). These VOCs will be emitted either by anthropogenic or biogenic sources. In general, the degradation and conversion processes lead to more water-soluble organic compounds, e.g., carboxylic acids. In the literature, the photo-induced oxidation pathway of pyruvic acid is described by two concepts (Guzman et al., 2006; Griffith et al., 2013; Reed Harris et al., 2014). The first one states the formation of lactic acid alkyl radicals, which react afterwards with molecular oxygen to peroxyl radicals with a rate constant of  $k \approx 10^9$  L mol<sup>-1</sup> s<sup>-1</sup>. (Griffith et al., 2013; Reed Harris et al., 2014) The other one assumes that, the peroxyl radical formation is a minor reaction pathway beside the alkyl radical addition reaction to pyruvic acid. A smaller rate constant of  $k = 1 \times 10^6 L mol^{-1} s^{-1}$  for the peroxyl radical formation was obtained. (Guzman et al., 2006) The difference in the rate constants of the oxygen addition is of about three orders of magnitude that clearly leads to different oxidation products and yields in aqueous solution. To clarify the difference in the rate constant of the oxygen addition, spectroscopic and kinetic investigations of the alkyl and peroxyl radicals have been performed by use of a laser photolysis - long path absorption (LP-LPA) setup. The temperature and pH dependent measurements of the H atom abstraction reaction by OH radicals of lactic acid k =  $(6.3 \pm 1.1) \times 10^8$  L mol<sup>-1</sup> s<sup>-1</sup>, lactate k =  $(8.9 \pm 0.8) \times 10^8$  L mol<sup>-1</sup> s<sup>-1</sup>, pyruvic acid k =  $(3.2 \pm 0.6) \times 10^8$  L mol<sup>-1</sup> s<sup>-1</sup> and pyruvate  $k = (7.1 \pm 1.8) \times 10^8 L \text{ mol}^{-1} \text{ s}^{-1}$  were performed, in order to characterize the first oxidation step. In the second step the electron transfer reaction of the ferricyanide with the lactic acid alkyl radical  $k = (4.3 \pm 0.4) \times 10^8 L$ mol<sup>-1</sup> s<sup>-1</sup> and the lactate alkyl radical  $k = (2.4 \pm 0.7) \times 10^8$  L mol<sup>-1</sup> s<sup>-1</sup> were determined. By using these reference constants the molecular oxygen addition reaction with lactic acid alkyl radical  $k = (2.2 \pm 0.1) \times 10^9 L \text{ mol}^{-1} \text{ s}^{-1}$  and the lactate alkyl radical k =  $(3.4 \pm 0.2) \times 10^9$  L mol<sup>-1</sup> s<sup>-1</sup> have been obtained. According these findings and the confirmation of the work of Adams and Willson, 1969, the estimated value of Guzman et al., 2006 (k  $\approx 10^6$  L mol<sup>-1</sup> s<sup>-1</sup>) appears to low.

#### Keywords

OH radical reaction, Peroxyl radical formation, Aqueous phase.
#### Introduction

Pyruvic acid can be formed in the troposphere either primarily the photooxidation of biogenic or anthropogenic precursors and can be found in both the gas and aqueous phase (Sempere et al., 1994; Veres et al., 2011). Previous and current studies on atmospherically relevant aqueous phase processes have focused on organic reactions with OH radicals, (Ervens et al., 2003, Schaefer et al., 2012) whereas the photolysis of organics, e.g. ketones and aldehydes might also play a role in SOA formation processes. (George et al., 2014)

However, the aqueous-phase photolysis of pyruvic acid including the resulting products is different from that in the gas-phase and is more controversial (Vesley and Leermakers, 1964; Guzman et al., 2006; Griffith et al., 2013; Reed Harris et al., 2014). In both concepts the triplet-state pyruvic acid reacts with another pyruvic acid molecule and form the lactic acid alkyl radical. The differences between the both concepts are in the subsequent reactions. The first one states that, the peroxyl radical formation is a minor reaction pathway beside the alkyl radical recombination reaction as well as the alkyl radical addition reaction to pyruvic acid. A smaller rate constant of  $k = 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  for the peroxyl radical formation was obtained (Guzman et al., 2006). The other one assumes that, the formation of lactic acid alkyl radicals, leads to peroxyl radicals by the addition with molecular oxygen with a rate constant of  $k \approx 10^9$ M<sup>-1</sup> s<sup>-1</sup> (Griffith et al., 2013; Reed Harris et al., 2014). The difference in the rate constants of the oxygen addition is of about three orders of magnitude that clearly leads to different major reaction pathways and results in different product distributions in the aqueous solution.

The aim of this work was to clarify the difference in the rate constant of the oxygen addition reaction of the formed alkyl radical.

#### **Experimentals**

The investigations of the kinetic of the OH radicals and of the alky radicals towards either ferricyanide  $(K_3[Fe(CN)_6])$  or molecular oxygen in an aqueous solution were conducted by using a Laser Flash Photolysis - Differential Amplified Laser - Long Path Absorption (LFP-DAL-LPA) setup.

Laser Flash Photolysis - Differential Amplified Laser - Long Path Absorption (LFP-DAL-LPA)

The LFP-DAL-LPA setup (Figure 1) is based on a continuous flow cell. The OH radicals were generated in a high-purity silica cell of 28 cm<sup>3</sup> volume by the photolysis at  $\lambda = 248$  nm of the precursor hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) initiated by an excimer laser (COMPEX 201, Lambda Physics). The White cell mirror configuration

was adjusted for 8 passes giving an absorption path length of 32 cm (White, 1942). A differential amplifier system with two photodiodes (S1336-44BQ, Hamamatsu) was used as the detector. The differential amplifier system was used to improve the signal-tonoise ratio (SNR) of the detected signal. The combination of a monochromator and a photodiode was used to avoid interferences due to scattered light from the excimer laser.



Figure 1. Scheme of the LFP-DAL-LPA system

The time dependencies of the formed radicals were observed at  $\lambda = 405$  nm in case of the OH radical competition kinetic or  $\lambda = 442$  nm in case of the alkyl radical competition kinetic. The concentration of the dissolved oxygen (O<sub>2</sub>) in the aqueous solution has been adjusted by flushing with argon gas and measured with a clark electrode (REK 1–1, Biolytik) which was connected to the measurement cell.

#### OH competition kinetics

The direct observation of the OH radicals is difficult, due to the low absorption in the deep UV (Herrmann et al., 2010) and the overlap absorption from other formed species e.g. alkyl or peroxyl radicals. To investigate the rate constant of an oxidation reaction of the OH radicals with organic reactants the common method of the competition kinetics with the rhodanide anion as reference reactant was used (Chin and Wine, 1992).

$$H_2O_2 + hv (248 nm) \longrightarrow 2 OH^{-}$$

$$OH^{-} + Reactant \longrightarrow R^{-} + H_2O$$

$$OH^{-} + SCN^{-} \iff SCNOH^{--}$$

$$SCNOH^{--} \iff SCN^{-} + OH^{-}$$

$$SCN^{-} + SCN^{-} \iff (SCN)_2^{--}$$

#### Ferricyanide Competition Kinetics

The reactivity of the alkyl radical towards dissolved oxygen was investigated by using a modified competition kinetic method (Schaefer et al., 2015).

$$\mathbf{R} \cdot + [\mathrm{Fe}(\mathrm{CN})_6]^3 \longrightarrow \mathbf{R}' + [\mathrm{Fe}(\mathrm{CN})_6]^4$$

<sup>•</sup> Correspondence to: schaefer@tropos.de

As reference reactant the ferricyanide (K<sub>3</sub>[Fe(CN)<sub>6</sub>]) was used, which reacts with alkyl radicals (R·) by electron transfer yielding the nonabsorbing ferrocyanide at  $\lambda = 442$  nm.

#### **Results and Discussion**

The H atom abstraction reactions of OH radicals with lactic acid, lactate, pyruvic acid and pyruvate were measured as a function of the pH and T in aqueous solution.



Figure 2. Temperature dependency of the OH radical reaction with lactic acid and lactate

The rate constants at T = 298 K and their corresponding Arrhenius parameters from the present work are summarized in Table 1.

Table 1. Summary of the obtained second	order	rate
constants and Arrhenius parameter	ers	

	OH radical		
	k298K /	Ea /	A /
	L mol <sup>-1</sup> s <sup>-1</sup>	kJ mol <sup>-1</sup>	L mol <sup>-1</sup> s <sup>-1</sup>
Lactic acid	$(6.3 \pm 1.1) \times 10^8$	$9\pm4$	$(2.7 \pm 0.2) \times 10^{10}$
Lactate	$(8.9\pm0.8)\times10^8$	$8\pm3$	$(2.7\pm 0.1)  imes 10^{10}$
Pyruvic acid	$(3.2\pm0.6)\times10^8$	$15\pm5$	$(1.1 \pm 0.1) \times 10^{11}$
Pyruvate	$(7.1\pm1.8)\times10^8$	$25\pm19$	$(1.5 \pm 0.4) \times 10^{13}$

The OH radical reactions of the carboxylic acids appear to be pH-dependent with a faster rate constant in the case of the deprotonated form of the acid. The H atom abstraction in the OH radical reaction occurs at the CH<sub>3</sub> group in the case of pyruvic acid/ pyruvate and at the CH group in the case of lactic acid/ lactate. The obtained rate constants and the activation parameters of the lactic acid/ lactate and pyruvic acid/ pyruvate are in a good agreement with literature values (Martin et al., 2009; Ervens et al., 2003).

In order to investigate the alkyl radical reaction with dissolved oxygen in the aqueous solution the protoneted and deprotoned form of the lactic acid was oxidized by OH radicals. The formed  $\alpha$ -hydroxy alkyl radical react with the ferricyanide in an electron transfer reaction to pyruvic acid and ferrocyanide. The averaged first-order rate constants derived from the change of the absorption at  $\lambda = 442$  nm during the bleaching reaction are linear to

the ferricyanide concentration (Figure 3). From the slope of the plot, the bimolecular rate constant of the lactic acid alkyl radical reaction with ferricyanide was determined  $(4.3 \pm 0.4) \times 10^8$  L mol<sup>-1</sup> s<sup>-1</sup>.



Figure 3. Determination of the reference rate constant for the bleaching reaction of the lactic acid alkyl radical with ferricyanide in the aqueous solution.

The rate constant of the lactate alkyl radical reaction with ferricyanide can be given with  $k = (2.4 \pm 0.7) \times 10^8$  L mol<sup>-1</sup> s<sup>-1</sup>. The obtained value of the lactate alkyl radical is factor 6 smaller than the value ( $k = 1.5 \times 10^9$  L mol<sup>-1</sup> s<sup>-1</sup>) given by Adams and Willson, 1969. In comparison the rate constant of the electron transfer reaction of the glycolate alkyl radical can be given with  $k = 5.0 \times 10^8$  L mol<sup>-1</sup> s<sup>-1</sup> (Adams and Willson, 1969).

The electron transfer reaction of the aforementioned alkyl radicals was used as reference constant in the competition reaction with dissolved oxygen. The linear regression with forcing to vertical intercept of 1 in Figure 5 leads to a rate constant for the reaction of the lactic acid alkyl radical with  $O_2$  of  $k = (2.2 \pm 0.1) \times 10^9$  L mol<sup>-1</sup> s<sup>-1</sup>.



Figure 4. Determination of  $k_{2nd}$  by plotting the ratio of the absorptions against the ratio of the concentrations in the case of lactic acid

In case of lactate alkyl radical the rate constant of the addition reaction with molecular oxygen can be calculated with  $k = (3.4 \pm 0.2) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  and is in good agreement with the rate constant  $k = 2.6 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  from Adams and Willson, 1969.

#### **Summary and Conclusion**

In this study the temperature and pH dependent measurements of the H atom abstraction reaction of either the protonated or deprotonated form of lactic acid or pyruvic acid by OH radicals were performed. Furthermore, the rate constant of O<sub>2</sub> addition to the lactic acid alkyl radical and the lactate alkyl radical by using the ferricyanide competition kinetic method was determined. The obtained rate constants can be given with  $k \approx 10^9$  L mol<sup>-1</sup> s<sup>-1</sup> of the molecular oxygen addition reaction, which confirms the work of Adams and Willson, 1969. Due to this, the estimated value of Guzman et al., 2006 ( $k \approx 10^6$  L mol<sup>-1</sup> s<sup>-1</sup>) appears to low, therefore the general suggested value of the molecular oxygen addition reaction k  $\approx 10^9$  L mol<sup>-1</sup> s<sup>-1</sup> should be used.



Figure 5. Revised photo-induced pyruvic acid oxidation mechanism from Reed Harris et al., 2014

According to the findings of this study the photoinduced pyruvic acid oxidation mechanism from Reed Harris et al., 2014 should be used.

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## TROPOSPHERIC AQUEOUS-PHASE OXIDATION OF ISOPRENE DEGRADATION PRODUCTS

Tobias Otto<sup>\*</sup>, Bastian Stieger, Thomas Schaefer and Hartmut Herrmann Leibniz Institute for Tropospheric Research – Leipzig Permoserstraße 15 04318 Leipzig, Germany

#### Abstract

The most common oxidizing agents in the atmosphere are radicals, such as hydroxyl, nitrate and sulfate as well as hydrogen peroxide and ozone as non-radical agents. The mentioned oxidizing agents are capable to degrade emitted volatile organic compounds (VOCs) to more oxidized and functionalized compounds. Caused by an increasing grade of oxidation and functionalization, these species become less volatile and more water soluble. These properties lead to an enrichment of the oxidized and functionalized species in aqueous particles and cloud droplets where further oxidation processes occur. Atmospheric models will benefit from the investigation of such processes to become more valuable. Isoprene is the most emitted biogenic VOC with a source strength of 500 - 750 Tg a<sup>-1</sup> (Guenther et al., 2006), besides methane. The first generation oxidation products of isoprene are methacrolein and methyl vinyl ketone, which are known to be dissolved in aqueous solution. Hence, the kinetics of their radical driven oxidation the one of their degradation products has been studied. Radical kinetic investigations are carried out with a laser flash photolysis - long path laser absorption (LFP - LPA) setup to determine second order rate constants and activation parameters. The obtained second order rate constant of the degradation products of methacrolein and methyl vinyl ketone, such as 2-Methyloxiran-2-carbaldehyd, 1-Oxiran-2-ylethanone and 2,3-Dihydroxy-2methylpropanal are in case of the sulfate radical in the range 10<sup>6</sup> to 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup>. The determined kinetic data of oxidation processes of these compounds will improve the understanding of the tropospheric oxidation mechanism of isoprene oxidation products in aqueous solution. The derived kinetic parameters will be implemented into multiphase atmospheric chemistry models such as CAPRAM (chemical aqueous phase radical mechanism).

#### Keywords

Radical reaction, Aqueous phase, Troposphere.

#### Introduction

Isoprene is the most important single source of biogenic volatile organic compounds (BVOCs), with a recently estimated global emission of 594  $\pm$  34 Tg a<sup>-1</sup> (Sindelarova et al., 2014). Atmospheric relevant factors, such as the ozone concentrations (Lam et al., 2013; Sakulyanontvittaya et al., 2015) as well as the formation of secondary organic aerosol (SOA) (Hallquist et al., 2009; Sakulyanontvittaya et al., 2015) are influenced by the chemistry of isoprene. Several studies concerning the chemistry of isoprene and its first oxidation products methacrolein and methyl vinyl ketone in the gas phase (Kroll et al., 2005; Hites and Turner, 2009; Iannone et al., 2009) were executed. Besides, these investigations, theoretical studies were performed to calculate thermodynamic properties of isoprene degradation processes, which enable a more precise description of formed oxidation products, mechanisms and the according yields.

Actual studies investigate the formation of epoxydiols in the gas phase (Paulot et al., 2009) that are discussed as SOA precursor. Even epoxides can also be of interest in the tropospheric aqueous phase, where the epoxides of methacrolein and methyl vinyl ketone can be formed or deposited from the gas phase. Studies of the oxidation of methacrolein in the aqueous phase indicate the appearance of intermediate epoxides (Liu et al., 2009; Schöne et al., 2014). Therefore, oxidation reactions of epoxide and subsequent diol species of methacrolein and methyl vinyl ketone with tropospheric relevant oxidizing agents, in particular hydroxyl radicals (OH), nitrate radicals (NO<sub>3</sub>) and sulfate radicals (SO<sub>4</sub><sup>-</sup>) have to be investigated. Consequently, the data of reaction kinetics and the formed oxidation products improve the understanding of the aqueous isoprene oxidation process, the estimation of the contribute to the SOA formation as well as the predictive capabilities of atmospheric models.

#### Experimentals

Kinetic measurements were carried using a laser induced photolysis to generate the reacting radicals. Formed radicals were observed via by multi-path absorption. The combination of both techniques form the Laser Flash Photolysis – Long Path Absorption setup (LFP–LPA), which is described in the following.

#### Laser Flash Photolysis – Long Path Absorption setup

The LFP-LPA setup in principle is a continuous through flowed measurement cell (depicted in Figure 1) irradiated by an pulsed excimer laser to generate the radicals. Depending on the investigated radical, the



Figure 1. Scheme of the measurement system

active medium of the laser was varied between KrF and XeF, to switch the photolysis wavelength from 248 nm to 351 nm. The time dependencies of the formed radicals were observed at  $\lambda = 473$  nm or  $\lambda = 635$  nm. In detail the analytical light was mirrored via a white cell optic (White, 1942) multiple times to gain a long path absorption. Further details can be seen in table 1 in below.

*Table 1. Summary of the measurement conditions*<sup>1</sup>

radical	OH	SO4 <sup>-</sup>	NO <sub>3</sub>
$\lambda_{Photo.}$ / nm	248	248	351
$\lambda_{Obs.}$ / nm	473	473	635
measurement	c. k.	d. m.	d. m.
method			
precursor	$H_2O_2$	$Na_2S_2O_8$	$Na_2S_2O_8/$
			NaNO <sub>3</sub>
$[H_2O_2] / M$	$2 \times 10^{-4}$		
$[Na_2S_2O_8] / M$		$2.5  imes 10^{-4}$	0.03
[NaNO <sub>3</sub> ] / M			0.1
[KSCN] / M	$2 \times 10^{-5}$		

#### Competition kinetics system

OH radicals show weak absorptions in the deep UV with a maximum of  $\epsilon_{OH, 230nm} = 570 \text{ M}^{-1} \text{ cm}^{-1}$  at 230 nm (Herrmann et al., 2010). Besides this, peroxyl radicals also absorb in this region of the electromagnetic spectrum. Therefore, the OH radical was observed via the SCN reference system described by Chin and Wine (1992). OH radicals react with SCN<sup>-</sup> following the subsequent mechanism

 $OH + SCN^- \rightleftharpoons SCNOH^-$ 

 $SCNOH^- \rightleftharpoons OH^- + SCN$ 

 $SCN + SCN^{-} \rightleftharpoons (SCN)_{2}^{-}$ 

competing with the reaction of the organic reactant and OH (Chin and Wine, 1992).

 $OH + organic reactant \rightarrow products$ 

Correspondence to: tobias.otto@tropos.de

<sup>&</sup>lt;sup>1</sup> c. k. = competition kinetics; d. m. = direct measurement

The absorption of the  $(SCN)_2^-$  anion  $(A_0)$  is observable at a wavelength of 473 nm. Every addition of an organic reactant lowers the absorption, resulting a absorption at this reactant concentration  $(A_X)$ .

#### **Results and Discussion**

Products studies by Schöne et al. (2014) proved the formation of the diol derivatives 3,4-dihydroxy-2butanone (II, Figure 2) and 2,3-dihydroxy-2methylpropanal (IV, Figure 2) in laboratory studies mimicking the tropospheric aqueous-phase oxidation of methacrolein and methyl vinyl ketone. Both the compounds II and IV are also suggested to be acid catalyzed ring opening products of the intermediate epoxide moieties 1-(2-oxiranyl)-ethanone (I) and 2methyl-2-oxiranecarboxaldehyde (III). Because of their atmospheric relevance, these oxidation products of methacrolein and methyl vinyl ketone were investigated regarding their reaction kinetics with hydroxyl, sulfate, and nitrate radicals.



Figure 2. Postulated mechanism toward the investigated compounds

In case of the OH radical reactions the rate constants are the product of the reference constant  $(k_{ref})$  of the rhodanide reference system provided by Chin and Wine (1992).

$$k_{ref}(T) = \exp\left((29.614 \pm 0.636) - \frac{1900 \pm 190}{T} K\right) M^{-1} s^{-1}$$

and the slope of the  $A_0$  /  $A_X$  against [reactant] / [SCN<sup>-</sup>] plot, depicted in Figure 3.

Second order rate constants of reactions of  $NO_3$  and  $SO_4^-$  are the slope of a linear regression of a plot of the first order rate constant against the concentration of the organic reactant. The obtained second order rate constants at a temperature of 298 K are summarized in Table 2. The calculated errors of the rate constants were

statistical with a student t-factor of 95% defined from the regression.



Figure 3. Determination of  $k_{2nd}$  by plotting the ratio of the absorptions against the ratio of the concentrations of the reactant and the rhodanide reference

In general the trend of reactivity is  $k_{2nd}(OH) > k_{2nd}(SO_4^-) > k_{2nd}(NO_3)$ . The sulfate rate constants of 1-(2-oxiranyl)-ethanone (I) is one order of magnitude lower compared to the one of 2-methyl-2-oxiranecarboxaldehyde (III).

Table 2. Summary of the determined second order rate constants at 298 K

constants at 200 K			
	OH radical	NO <sub>3</sub> radical	SO4 <sup>-</sup> radical
	k <sub>2nd</sub> /	k <sub>2nd</sub> /	k <sub>2nd</sub> /
	$L \mod^{-1} s^{-1}$	L mol <sup>-1</sup> s <sup>-1</sup>	$L \text{ mol}^{-1} \text{ s}^{-1}$
Ι	$(1.29 \pm 0.44)$	-	$(6.90 \pm 1.99)$
	$ imes 10^8$		$ imes 10^{6}$
III	-	$(4.76 \pm 1.09)$	$(2.31 \pm 0.10)$
		$ imes 10^{6}$	$ imes 10^7$
IV	-	$(7.94 \pm 0.60)$	$(3.25 \pm 0.15)$
		$ imes 10^{6}$	$ imes 10^7$

In all cases the second order rate constants were temperature-dependent determined in a temperature range of 278 K to 318 K. Subsequently, activation parameters were calculated by the analysis of the linear regression of the Arrhenius plot (Figure 4).



Figure 4. Arrhenius plot of the reaction of OH radicals with 1-(2-oxiranyl)-ethanone at pH ~ 6

#### **Summary and Outlook**

The study exhibits that the reaction with OH radicals is the main degradation path way, caused by the high second order rate constant, which is one to two orders of magnitude higher than the ones for sulfate or nitrate reactions. The mentioned general trend of the second order rate constants:  $k_{2nd}(OH) > k_{2nd}(SO_4) > k_{2nd}(NO_3)$ is, as it was expected concerning former investigations of radical reactions (cf. Schöne et al. (2014)). The obtained data complete the kinetic data set of the tropospheric oxidation mechanism of the first generation oxidation products, methacrolein and methyl vinyl ketone, but not completely at this stage.

In the future, the kinetic data can be implemented in atmospheric chemistry models, such as CAPRAM to improve the predictive capabilities.

The ongoing work will also include product studies of the OH radical-driven oxidation reactions of the kinetically investigated compounds mentioned in the results and discussion section to enhance the understanding of the tropospheric isoprene oxidation mechanism, especially the oxidation of the degradation products in the tropospheric aqueous phase.

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## RECENT ADVANCES IN STUDYING THE MECHANISM OF PHOSPHA-MICHAEL ADDITION OF TERTIARY PHOSPHINES TO ELECTRON-DEFICIENT ALKENES

Alexey V. Salin\*, Albert R. Fatkhutdinov, Anton V. Il'in, Fanuza G. Shamsutdinova Kazan Federal University 18 Kremlevskaya Str., Kazan, 420008, Russia

#### Abstract

The Michael-type addition of tertiary phosphines to electron-deficient alkenes is a convenient way to generate reactive phosphonium zwitterionic intermediates, which participate readily in many synthetically useful transformations. Our kinetic data provide evidence that proton transfer to carbanion centre of intermediate zwitterion is the rate-determining step (RDS) in quaternization reactions of tertiary phosphines with electron-deficient alkenes in the presence of a proton source. This conclusion is based on: (i) a 3<sup>rd</sup>-order rate equation which includes the concentration of proton source; (ii) the absence of a correlation between the rate constant and the electrophilicity of the alkene together with very strong dependence of the rate on the basicity of solvent; (iii) solvent isotope effect for the reactions in deuteroacetic acid. That a proton transfer is the RDS is due to the tendency of the zwitterion to reconvert to the reactants with the energy barrier being lower than that for proton transfer; this conclusion was confirmed by DFT calculations at the B3LYP/6-31+G(d,p) level. Effect of anchimeric assistance was revealed for the reactions of tertiary phosphines with maleic and *cis*-aconitic acids. The absence of such effect for the *trans*-isomeric acids provides evidence to a crucial role of intramolecular P····O interaction in stabilizing the phosphonium zwitterions.

#### Keywords

Conjugate addition, Rate-determining step, Solvent isotope effect, Anchimeric assistance.

#### Introduction

During the past decades, the Michael-type addition of tertiary phosphines to electron-deficient alkenes has found numerous applications in chemistry. The ability of tertiary phosphines to attack electrophilic carbon-carbon double bonds and furnish reactive phosphonium zwitterionic intermediates is widely used in catalytic transformations, for example, in the Morita-Baylis-Hillman and the Rauhut-Currier reactions, to construct carbon-carbon and carbon-heteroatom bonds by coupling of these zwitterions with electrophilic partners, such as aldehydes, imines and activated alkenes (Methot and Roush, 2004). Water-soluble hydroxyalkyl phosphines were found to be excellent bleaching and brightness stabilization agents for pulps, and the Michael-type addition of such phosphines to conjugated carbonyl components of lignin is also involved in this process (Moiseev et al., 2007). Stable addition products of tertiary phosphines to electrondeficient alkenes, quaternary phosphonium salts, attract (Werner, organocatalysts attention as 2009). surfactants, and biologically active substances. Although the synthetic usefulness of the phospha-Michael addition has been largely demonstrated,

knowledge on the kinetics and mechanism of this reaction is sparse. Clearly, further information on this topic is necessary for optimization of the reaction conditions and may help to overcome negative features of the phosphine-catalyzed reactions, such as low conversion rates, highly substrate-dependent product yields, and difficulties in controlling selectivity. To fill up the gap in the theory of the phospha-Michael addition, we have recently initiated a systematic study of the mechanism of quaternization of tertiary phosphines with electron-deficient alkenes in the presence of a proton source. This paper summarizes our contribution to the unraveling the mechanism of this phospha-Michael addition.

#### **Results and Discussion**

Prerequisite for our kinetic study became synthetic investigation of the reaction of tertiary phosphines with unsaturated carboxylic acids (Scheme 1) (Galkin et al., 2006). Our group was interested in efficient synthesis of carboxylate phosphobetaines of type **1**, which can be considered as phosphorus analogs of amino acids with a potentially wide spectrum of practically useful properties. The synthetic study revealed that the reaction products can be obtained

<sup>•</sup> To whom all correspondence should be addressed, E-mail: salin555@mail.ru

either as phosphonium salts **2**, in which negative ion is the anion of the starting unsaturated carboxylic acid, or as carboxylate phosphobetaines **1**, whose carboxylate centre is bonded to a proton-donor molecule, for example, a molecule of water.



 $R^1$  = H, Me, Ph, 4-ClC<sub>6</sub>H<sub>4</sub>, 4-MeOC<sub>6</sub>H<sub>4</sub>, CO<sub>2</sub>H; R<sup>2</sup> = H, Me, CH<sub>2</sub>CO<sub>2</sub>H

#### Scheme 1. The reaction of tertiary phosphines with unsaturated carboxylic acids

Initially, the role of a proton-donor unit was attributed to stabilization of carboxylate centre of phosphobetaine formed via [1,3]-intramolecular proton shift within zwitterionic intermediate **3**. To shed more light on the mechanism of this reaction, we started the kinetic study. When an aromatic tertiary phosphine is used as reactant, the reaction kinetics can be monitored readily by spectrophotometry under condition of pseudo-first order in the phosphine.

We found that the quaternization process is always described by a 3<sup>rd</sup>-order kinetic equation, whose form depends on the nature of solvent. In the medium of strong proton-donor solvents, such as carboxylic acids (acetic, propionic acids), the proton transfer proceeds from the solvent, and the rate is described by Eq. (1) (Galkin et al., 2009).

 $rate = k_{obs} [PR_3] [acid] [solv]$ (1)

Here,  $[PR_3]$  is the concentration of tertiary phosphine; [acid] is the concentration of unsaturated carboxylic acid; [solv] is the concentration of protondonor solvent. The 3<sup>rd</sup>-order kinetic equation of type (1) was also found to be applicable for quaternization reaction of tertiary phosphines with functional derivatives of unsaturated carboxylic acids, esters, acrylonitrile, and acrylamide, in the medium of protic solvent (acetic acid) (Salin et al., 2013).

In case of the quaternization of tertiary phosphines with unsaturated monocarboxylic acids in aprotic solvents, the proton transfer proceeds from the second molecule of the acid, and rate Eq. (2) holds true (Salin et al., 2014).

 $rate = k_{obs} [PR_3] [acid]^2$  (2)

For alcohols the rate equation has the form of superposition [Eq. (3)] with two parallel intermolecular pathways of proton transfer: from the solvent and the second molecule of unsaturated acid (Salin et al., 2010).

rate = 
$$k_{obs,1}$$
[PR<sub>3</sub>][acid][solv]+  
+ $k_{obs,2}$ [PR<sub>3</sub>][acid]<sup>2</sup> (3)

The kinetic data obtained for the reaction of tertiary phosphines with electron-deficient alkenes allowed us to propose a stepwise mechanism, which includes reversible formation of zwitterionic intermediate **3a**, followed by rate-determining proton transfer to the generated carbanionic centre from a proton donor solvent or a second molecule of unsaturated acid (Scheme 2).

 $\mathsf{PR}_3 + \mathsf{PR}_3 \mathsf{PR}_3 \mathsf{PR}_4 \overset{k_1}{\underset{k_{-1}}{\longrightarrow}} \mathsf{R}_3 \mathsf{P} \overset{\oplus}{\underset{\mathbf{Sa}}{\longrightarrow}} \mathsf{EWG}$ 



EWG = CO<sub>2</sub>H, CO<sub>2</sub>Me, CN, CONH<sub>2</sub>; solvent: AcOH

$$\begin{array}{c} \overset{@}{\operatorname{Hop}} & \overset{@}{\operatorname{Hop}} & \overset{@}{\operatorname{Hop}} & \overset{W}{\operatorname{Hop}} & \overset{W}{\operatorname{Hop}}$$

#### Scheme 2. Mechanism proposed for the phospha-Michael reaction of tertiary phosphines with electrondeficient alkenes

Although the proposed mechanism explained well, why the phosphonium salts are usually formed instead of carboxylate phosphobetaines in the reaction of tertiary phosphines with unsaturated carboxylic acids, the conclusion about the rate-determining protonation of carbanionic center in acidic media seemed quite surprising, and further evidence were required. Another interesting reaction feature was the fact that [1,3]-intramolecular proton shift in the generated zwitterion **3** was never realized, in spite the proximity of its highly basic carbanionic center to the acidic carboxyl group, and another proton source was essential for the reaction completion.

Having determined the kinetic data for the reaction of PPh<sub>3</sub> with acrylic acid in a series of 15 aprotic solvents (Table 1), we analyzed the solvent effect using linear free energy relationship on the basis of one- and multiparameter equations, such as the Kamlet-Taft, the Catalán, the Gutmann-Mayer, and the Koppel-Palm equations (Salin et al., 2014). The results obtained showed that the solvent basicity defined in any of the scales has the dominant and negative effect on the reaction rate confirming the assignment of the rate-determining step to the proton transfer. The best result gave a two-parameter model constructed on the basis of the Reichardt polarity  $E_{\rm T}$  and the basicity *B* from the Koppel-Palm equation, with weak positive

effect of the  $E_{\rm T}$  parameter on the reaction rate and very strong negative effect of the *B* parameter [Eq. (4)].

$$\log k_{\rm III} = -1.7 + (6.0 \pm 4.7) \cdot 10^{-2} E_{\rm T} - -(1.40 \pm 0.26) \cdot 10^{-2} B \tag{4}$$

$$N = 15, \ R = 0.961, \ s = 0.078$$

*Table 1. Rate constants for the reaction of PPh<sub>3</sub> with acrylic acid in aprotic solvents (30 °C)* 

Solvent	$10^3 k_{\rm III},  {\rm M}^{-2}  {\rm s}^{-1}$
Propylene carbonate	93.1
Acetonitrile	56.9
Propionitrile	55.2
Sulfolane	40.3
Diethyl carbonate	25.4
Ethyl formate	13.2
1,3-Dioxolane	10.7
Butyl acetate	10.6
Methyl acetate	9.83
Ethyl acetate	9.14
1,2-Dimethoxyethane	2.03
1,4-Dioxane	1.67
THF	0.742
DMF	0.138
DMSO	0.081

Further evidence on the mechanism was reflected by analysis of the relative reactivities of the electron-deficient alkenes (Salin et al., 2013), where typically the more electrophilic species react more readily with tertiary phosphines (Methot and Roush, 2004). However, the data of Table 2 show, for example, that acrylonitrile activated by the strongest electron-withdrawing CN group is the least active, and acrylic acid, which is of very similar electrophilicity to methyl acrylate, is about ten times more reactive than the ester. The lack of correlation means that nucleophilic attack of the phosphine is not the ratedetermining step; this is consistent with the rate equation (1), in which proton transfer is ratedetermining. Low reactivity of acrylonitrile can be explained taking into account that with carbonylcontaining substrates, the zwitterion can be stabilized by an intramolecular P...O interaction, whereas a P...N interaction via a nitrile group is impossible (Scheme 3).

# Scheme 3. Phosphonium zwitterions derived from carbonyl-containing alkenes and acrylonitrile

The higher reactivity of the carboxylic acids (Table 2) could result from additional stabilization of

the zwitterion by intermolecular H-bonding involving the acetic acid solvent (Figure 1).



## Figure 1. Stabilization of phosphonium zwitterion by intermolecular H-bonding with acetic acid

One more evidence for a rate-determining protonation was provided by the solvent isotope effect (SIE) when AcOD was used as solvent (Table 2) (Salin et al., 2013). The measured SIE values are not very high (1.13-1.69), since they refer to a combined  $Kk_2$  term (Scheme 2) and reflect a compensation of a normal SIE of the second (rate-determining) step by an inverse SIE of the first equilibrium step.

To rationalize the rate-determining protonation of carbanionic centre in the studied reaction it seemed us reasonable to analyze its energy profile using DFT calculations (Salin et al., 2013). At the B3LYP/6-31+G(d,p) level, we studied the reaction mechanism in bimolecular variant in the absence of any proton source except for the reacting molecule of unsaturated carboxylic acid, and also examined the reaction in the presence of a third proton-donor molecule, a molecule of water. The reaction of PMe<sub>3</sub> with acrylic acid in gas phase was used as a model.

The results showed that [1,3]-intramolecular shift of carboxyl proton to carbanionic centre of the generated zwitterionic intermediate 3 was kinetically forbidden ( $\Delta G^{\neq}=33.5$  kcal mol<sup>-1</sup>), and external protondonor source was essential to complete quaternization. Although water-assisted proton transfer was about 5 times energetically more favorable than alternative intramolecular proton shift, the corresponding transition state was still the point with the highest energy on the surface, and according to definition, this step is the rate-determining in the reaction. The reason why fairly easy protonation of carbanionic centre of zwitterion 3 appears to be the rate-determining lies in high instability of this intermediate and its tendency to decompose to the starting reactants with a very small energy barrier, predicted to be only 0.5 kcal mol<sup>-1</sup>. Nucleophilic attack of phosphine is, however, the slowest step in this reaction. The calculations revealed that electrostatic interaction between phosphonium centre and carbonyl oxygen atom plays a significant role in stabilization of the generated zwitterion.

During the kinetic studies, effect of anchimeric assistance (a rate increase due to neighboring group participation) was revealed for the reaction of tertiary phosphines with maleic and *cis*-aconitic acids (Salin et al., 2014). Similar effect for *trans*-isomeric acids was not observed. We assumed that the unusual reactivity of *cis*-isomeric acids comes from additional stabilization of the resulting zwitterion by an intramolecular hydrogen bond. For example, the initial geometry of maleic acid favors stabilization of the zwitterion both by an electrostatic P…O interaction and intramolecular hydrogen bonding (Figure 2, A).

Table 2. Kinetic data for reactions of PPh<sub>3</sub> with electron-deficient alkenes in acetic and d<sub>1</sub>-acetic acid (30 °C)

Alkene	$10^3 k_{\rm III},  {\rm M}^{-2}  {\rm s}^{-1}  ({\rm AcOH})$	$10^3 k_{\rm III},  {\rm M}^{-2}  {\rm s}^{-1}  ({\rm AcOD})$	SIE
Maleic acid	99.5	77.1	1.29
Acrylic acid	8.17	7.20	1.13
Fumaric acid	3.12	-	-
Methyl acrylate	0.884	-	-
Acrylamide	0.624	0.370	1.69
Acrylonitrile	0.156	0.136	1.15

At the same time, the  $P \cdots O$  interaction in zwitterions derived from fumaric acid hinders free rotation around the  $C_{\alpha}$ - $C_{\beta}$  bond, making stabilization by intramolecular hydrogen bonding impossible (Figure 2, B).



Figure 2. Proposed difference between zwitterions generated from PPh<sub>3</sub> and maleic/fumaric acids

To assess the presented hypothesis, we studied kinetics of the reaction of PPh<sub>3</sub> with dimethyl maleate and dimethyl fumarate, using acetic acid as a solvent, since intramolecular hydrogen bonding in esters a priori is impossible. The study revealed that maleic ester is even less reactive than fumaric ester in this reaction confirming that the high reactivity of maleic acid arises from additional stabilization of the reaction intermediate by intramolecular hydrogen bonding.

#### Conclusion

The rate-determining step in the phospha-Michael reaction of tertiary phosphines with electrondeficient alkenes in the presence of a proton source is proton transfer to the carbanionic centre of the zwitterionic intermediate, as evidenced by: (i) a  $3^{rd}$ order rate equation that includes the concentration of a third (proton-donor) reagent; (ii) the absence of a correlation between the rate constant and the electrophilicity of the alkene, together with a very strong dependence of the rate on the general basicity of the solvent; (iii) solvent isotope effects for the reactions carried out in monodeuterated acetic acid; (iv) DFT computation of the reaction energy surface for.

The presented study shed light on structural features and stability of key intermediates of phosphine-catalyzed reactions of unsaturated electrophilic reagents. A crucial role of the intramolecular electrostatic  $P \cdots O$  interaction in stabilizing the phosphonium zwitterions was confirmed both by experimental and theoretical findings. That a proton transfer is the rate-determining step is due to the tendency of the intermediate zwitterion to reconvert to the reactants with the energy barrier being lower than

that for proton transfer. Isolation and characterization of such intermediates will thus prove to be extremely difficult.

#### Acknowledgments

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## CFD SIMULATIONS OF THE ISO-OCTANE IGNITION IN A RAPID COMPRESSION MACHINE USING DETAILED CHEMISTRY

N. Bourgeois<sup>\*1,2</sup>, F. Contino<sup>2</sup>, H. Jeanmart<sup>1</sup>

<sup>1</sup> Université catholique de Louvain (UCL), Institute of Mechanics, Materials and Civil Engineering, 1348 Louvain-la-Neuve, Belgium <sup>2</sup> Vrije Universiteit Brussel (VUB), Department of Mechanical Engineering, 1050 Elsene, Belgium

#### Abstract

The Rapid Compression Machine (RCM) is widely used in the study of auto-ignition phenomena at temperature and pressure conditions similar to those of standard combustion devices such as an internal combustion engine. A reactive and homogeneous mixture is rapidly compressed by a moving piston: the subsequent auto-ignition provides information that help developing detailed chemical kinetics models. The machine-to-machine variability observed in the experimental results is however a key question that needs to be definitely addressed as it is still an active topic of discussion in the RCM community. In this study, CFD simulations first for non reactive investigations, and then coupled to detailed chemistry for the ignition of iso-octane will highlight the strong machine-dependence of RCM experiments.

#### Keywords

Rapid Compression Machine (RCM), CFD, detailed chemistry, iso-octane, TDAC.

#### Introduction

Rapid Compression Machines have been extensively used in the past decades and are still nowadays to investigate auto-ignition phenomena. Although many research groups contribute to the pool of experimental data and to the development of kinetic mechanisms, two key questions related to experimental data remain pending and limit all the valuable information that could be extracted from the RCM experiments. The first point concerns the comparability from machine to machine. As illustrated by Figure 1, the auto-ignition delays measured for the iso-octane on different RCMs exhibit a significant variability, especially in the range of end-compression temperatures relevant for internal combustion engines (1000/T = 1.15...1.50). The second question is about the shot-to-shot repeatability for a same machine. The first question is addressed by fundamentally physical and the chemical understanding the phenomena arising within RCMs, as well as their interactions. Wall-resolved RANS (Reynolds Averaged Navier-Stokes) simulations coupled to detailed mechanisms are suited for such a study. The wallgenerated vorticity likely to induce the roll-up of a vortex inside the chamber and the wall-heat transfer are indeed phenomena located in the wall region that need to be accurately captured due to the strong influence they will exert on the fuel ignition.

Despite the machine-dependence of RCM experiments has already been evidenced (Mittal, 2008), no study aiming to address this specific question is to be mentioned. Lee and Hochgreb (1998) already recommended resort to a creviced piston in order to avoid the roll-up of the vortex which causes undesirable temperature inhomogeneities inside the combustion chamber. Würmel and Simmie (2005)



Figure 1. Iso-octane auto-ignition delays as a function of the adiabatic core temperature (i.e., the supposed temperature at the end of the compression stroke) for different RCMs. All data have been normalized to  $Y_{02} =$ 21%,  $\phi = 1$  and p = 10 atm (for more details, see Goldsborough, 2009).

studied extensively the influence of the piston geometry and ended up with an optimal crevice configuration. In the present study, reasons explaining machine-to-machine variability will be further described as exhaustively as possible. Some considerations about heat loss that were previously lacking are made.

Mittal and Sung (2006) demonstrated with experimental data how the ignition delays are influenced by the piston profile. Reactive simulations have been undertaken in a few studies, but systematically using mechanisms containing a moderate number of species: Mittal *et al.* (2008, 2010) investigated the ignition of the hydrogen (11 species, 19 reactions) and of the n-heptane (skeletal mechanism with 43 species and 185 reactions). In this study, a detailed description of the iso-octane kinetics aiming to

<sup>\*</sup>nicolas.bourgeois@uclouvain.be

accurately capture the specific NTC (Negative Temperature Coefficient) behavior of this primary fuel is used, namely the LLNL mechanism containing 874 species and 3796 reactions (Mehl *et al.*, 2009).

#### Numerical tools

The investigated geometry is the doublepiston machine of the Argonne National Laboratory. This machine is pneumatically driven and hydraulically damped (Goldsborough et al., 2011). Figure 2 illustrates how the 2-D axisymmetric mesh resolution is increased close to the walls. An additional symmetry boundary condition is applied on the top edge of the geometry due to the opposed piston configuration of this machine. All simulations are carried out using the free CFD library OpenFOAM. A tool specifically designed for RCM simulations has been developed. It allows taking the piston stroke that is specific to each machine as an input. A new mesh is generated each time it is compressed by a user-defined factor in order to keep an acceptable aspect ratio. The classic compressible RANS equations are solved and it is made use of the k- $\omega$ -SST turbulence model that is performing properly both in highly and weakly turbulent regions (Menter, 1993).



Figure 2. Mesh at TDC for non reactive simulations (40,000 cells, with 300,000 cells at BDC). Reactive simulations are done with a coarser mesh, still wall-resolved, due to CPU time constraints (16,000 cells at BDC and 9,000 cells at TDC).

Due to the computational burden associated to a direct resolution of the kinetics equations, some reduction techniques have to be employed. Such strategies essentially act on two aspects: the reduction of the mechanism (see e.g. Liang *et al.* and He *et al.*) aiming essentially at selecting on-the-fly a set of active species, and the tabulation of previously computed results (Pope, 1997). We take advantage of those two approaches using the TDAC (Tabulation of Dynamic Adaptive Chemistry) algorithm, mitigating the impact of the number of species and of the number of cells on the computational cost (Contino *et al.*, 2011). The tool has shown its efficiency in particular for single cylinder HCCI engine studies (e.g. Contino 2014).

#### **Results and discussion**

Several factors can explain the discrepancies we observe between different machines. For technical and practical reasons, direct measurement of temperature is challenging in RCMs (Desgroux, 1995). Most authors assume that a core being adiabatically compressed is formed inside the chamber and away from the thermal boundary layer, which allows to deduce the adiabatic core temperature  $T_C$  from the pressure measurement:

$$\int_{T_0}^{T_c} \frac{\gamma}{\gamma - 1} \frac{dT}{T} = \log\left(\frac{p_c}{p_0}\right),\tag{1}$$

with  $\gamma$  the specific heat ratio,  $p_0$  and  $p_c$  the pressures at bottom and top dead centers. Plotting the auto-ignition delay as a function of this core temperature gives valuable information, for instance making clearly appear the particular NTC region of a fuel, but it also conceals all the machine specificities, meaning that a same adiabatic core temperature for two different machines does not guarantee at all to have the same ignition delay. We identify three main reasons that can explain a constant bias between two facilities:

- the validity of the adiabatic core hypothesis is conditioned to the homogeneity of the temperature field inside the chamber. The ability of the crevices to efficiently absorb the thermal boundary layer during the piston displacement thus plays a key role. If the width of the channel leading to this crevices zone is badly dimensioned, the cold gases from the walls will tend to be moved towards the center of the chamber, which will not be reflected on a plot like that of Figure 1.
- The heat losses during the post-compression phase also have a significant impact on the auto-ignition delay. They will strongly affect the combustion duration due to the modification of the temperature evolution and homogeneity inside the combustion chamber.
- The piston compression trajectory can be quite different from a machine to another. As the combustion kinetics can already be initiated during the compression, the impact on the ignition delay can be significant.

The impact of the machine design (i.e., the piston geometry and the piston stroke) is significant within this context. All those fundamental reasons are illustrated first by non reactive simulations and then by reactive simulations.

#### Non reactive results

Prior to any analysis, it is important to notice that the experimental and simulated non reactive pressures for the Argonne RCM fit very well (Figure 3), showing that the wall heat transfer is properly captured during and after the compression phase. The end-compression temperatures computed according to Eq. (1) also agree with the maximum temperatures observed in the RANS simulations (Figure 4).



Figure 3. Experimental and simulated pressures for the Argonne RCM. Non reactive case.



Figure 4. Simulated maximum and averaged chamber temperatures compared to the  $T_C$  computed from the experimental pressure traces. The ten investigated case are located inside or close to the NTC region.

The ability of a creviced piston to make the incylinder temperature field more homogeneous is clearly observed on Figure 5. The large vertical motion coming from the flat piston profile must be avoided in the context of RCM experiments and the crevices are performing very well to do so. As already mentioned, the wall-heat transfer also plays a key role in RCM experiments. As a first thought, it could be expected that piston geometries with crevices will have a temperature decreasing faster as more heat is transferred to the walls due to a larger surface to volume ratio. This is only partially true: the global heat losses will be superior in that case, leading to a faster pressure decrease. But what really matters is what is happening inside the combustion chamber. Simulations clearly show enhanced fluid motions inside the chamber in the case of a flat piston (Figure 6). This will induce much more convective heat losses as the thermal boundary layer is getting thinner at those places. The effects on the chamber temperature as well as on its global homogeneity are unwanted. Therefore the benefits of using a creviced piston are actually double: in addition to a more homogeneous



Figure 5. Temperature fields [K] at TDC for flat and creviced pistons. Saturated colorbar (wall temperature is 328K).



*Figure 6. Radial velocity fields* [*m*/*s*] *for flat and creviced pistons at TDC.* 

temperature field, it also reduces the heat transfer to the wall inside the combustion chamber.

#### Reactive results

As was done for the non reactive simulations, it is aimed first to bring some evidence of the numerical tool capability to reproduce the experimental pressure traces of the iso-octane ignition. Nevertheless, the results of the CFD simulations combined with detailed chemistry are surprising and require some attention. As shown by Figure 7, the auto-ignitions obtained from the simulations are far from the experimental results. The global trend is that the delay is decreasing with the end-compression temperature. The NTC behavior fails to be reproduced. This is of course questioning, especially when being compared with classic 0-D simulations that agrees much better with the experimental data. The 0-D simulations are taking into account the compression effect as well as the heat loss thanks the widely used volume expansion approach that was initially described by Tanaka et al. (1995). Considering a more refined description of the physical phenomena occurring inside the RCM thus gives unsatisfying results. Those unexpected output have to be further explained and understood, and the possible reasons for that shall be further investigated.



Figure 7. Iso-octane auto-ignition delay as a function of the adiabatic core temperature.

#### Conclusions

Anything affecting the temperature field homogeneity and the wall heat transfer inside a RCM will also have an influence on the chemical kinetics. In this context, the piston geometry impact has been demonstrated with RANS simulations of both a creviced and a flat piston geometries. Results for reactive simulations will require additional investigation.

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## IMPROVING LABORATORY REACTORS: COMPUTATIONAL FLUID DYNAMICS AND DETAILED CHEMICAL KINETICS

Pieter A. Reyniers\*, Carl M. Schietekat\*, Stamatis A. Sarris\*, Kevin M. Van Geem\*, Guy B. Marin\* Laboratory for Chemical Technology, Ghent University Technologiepark 914, B-9052 Zwijnaarde (Ghent), Belgium

#### Abstract

Computational fluid dynamics simulations have been used to optimize the design of a jet stirred reactor for studying intrinsic kinetic studies of gas phase and surface reactions. First *in silico* residence time distribution experiments have been carried out at 900 K to assess the degree of non-uniformity on the macro mixing scale. The configuration of the jets respective to the gas outlet was optimized to minimize short-cut streams. The different nozzle orientations only have a minor effect on the pressure drop. Reactive simulations of ethane cracking in the three selected geometries revealed that the 45° case exhibits the highest temperature homogeneity and is thus the optimal configuration for kinetic studies of coke formation under steam cracking conditions.

#### Keywords

Computational fluid dynamics, Jet stirred reactor, Detailed chemical kinetics

#### Introduction

Laboratory reactors have played an important historical role in the development of modern-day science. Experiments on lab-scale form the basis for development of new processes and products as this drastically reduces cost. Moreover, high throughput testing allows to speed-up development. The ideally mixed reactor is a popular type of laboratory reactor for gas phase kinetics studies, in particular as an alternative for closed vessels, tubular reactors or burners (Battin-Leclerc et al., 2013). Inherent to this type of reactor is the quasi-homogeneous composition of the process gas in the reactor and in the outlet when it is operated at steady state. Analytical devices such as gas chromatographs and mass spectrometers can thus be easily coupled with an ideally mixed reactor to provide information about the process gas composition inside the reactor.

The jet stirred reactor (JSR) is an example of a reactor that can potentially be considered as an ideally mixed reactor. Here mixing is established using the kinetic energy of the process gas itself. It is injected at high velocity through a number of nozzles mounted centrally in the reactor. The so-called jets formed by the nozzles induce intense internal recycle streams, which are a prerequisite for homogeneous mixing. The relatively high pressure drop over the nozzles is not a problem for lab-scale reactors. Several jet stirred reactor designs are known, including those developed at the Massachusetts Institute of Technology (Longwell and Bar-Ziv, 1989), the Institute for Energy Technology ETH Zürich (Bengtsson et al., 1998),

the University of Leeds (Abdalla et al., 1982), Institut National Polytechnique de Nancy (Matras and Villerma, 1973), Centre de Recherches sur la Chimie de la Combustion et des Hautes Températures CNRS Nancy (Dagaut et al., 1986), Institut für Technische Verbrennung (ITV), RWTH-Aachen (Stoehr et al., 2015) and the Laboratory for Chemical Technology, Ghent University (Muñoz Gandarillas et al., 2014a, b). This type of reactor has often been used to study gas phase oxidation reactor and thermal decomposition reactors. Parametric studies in terms of inlet composition, temperature, pressure and residence times allow to acquire a dataset which can subsequently be used for parameter fitting in kinetic models or for validating *ab initio* models.

A diagram of a jet stirred reactors used for kinetic studies is shown in Figure 1.



Figure 1. Diagram of a jet stirred reactor.

<sup>•</sup> To whom all correspondence should be addressed: Prof. dr. ir. Kevin M. Van Geem, Kevin.VanGeem@UGent.be

Free jets have been the subject of extensive research over the past decades for their relevance in chemical reactors and in (non-premixed) combustion applications. David and Matras (David and Matras, 1975) published the condition of Liepmann and Laufer used to determine whether a jet can be considered as free. In traditional jet stirred reactor designs, this criterion is always satisfied for reactors with a diameter larger than 0.01 m. Hinze and Van Der Hegge Zijnen (Hinze and Van Der Hegge Zijnen, 1949) developed an analytical expression based on experiments describing the velocity in an axisymmetric free jet. Based on this work, Herbinet and Dayma (Battin-Leclerc et al., 2013) determined that the homogeneity of the process gas in a jet stirred reactor is sufficient if the following criteria are met:

1. the velocity of the jets at the nozzle exit should be sufficiently high to have fully developed turbulent flow. A Reynolds number is defined and experiments showed that mixing is sufficiently good for Re larger than 800. This results in an upper limit for the residence time  $\tau$  (Eq. (1)).

$$\operatorname{Re} = \frac{4\rho A R^{3}}{6\eta d \tau \tan(\beta)} \implies \tau \le \frac{\rho A R^{3}}{230\eta d}$$
(1)

2. the jets must induce intense internal recycle streams. Experimentally it is found that the recycle ratio  $R_r$  should be larger than 30 to have good mixing, resulting in a criterion for the ratio of the reactor diameter and the nozzle diameter (Eq. (2)).

$$R_r = \frac{\pi AR}{2d} \quad \Rightarrow \quad \frac{R}{d} > 64 \tag{2}$$

3. the exit velocity of the jets should not exceed the speed of sound resulting in a lower limit on the residence time (Eq. (3)).

$$\tau \ge \frac{4}{3} \frac{R^3}{d^2 c_{sound}(T, P)} \tag{3}$$

Ayass (Ayass, 2013) recently performed residence time distribution experiments and high speed camera analyses on different jet stirred reactor configurations homogeneity. to assess their gas phase The experimental results were validated using computational fluid dynamics (CFD). Stoehr et al. (Stoehr et al., 2015) experimentally measured a residence time distribution profile with methane as tracer gas at 600 K and verified mixing using an isothermal CFD simulation. They concluded that the reactor does not have the hydrodynamic properties of a ideally mixed reactor but rather of a well-stirred reactor. Up to now, to the best of the authors' knowledge, experiments and simulations have always been carried out in the absence of chemical reactions. It must be clear that the reactions significantly affect the hydrodynamic behavior because of expansion or contraction of the gas and/or due to their endo- or exothermicity. This implies that the results of an analysis at non-reactive conditions cannot be straightforwardly extrapolated to reactive conditions.

To illustrate this three alternative designs have been investigated under ethane steam cracking conditions (1100 K; 0.1 MPa). differing in the orientation of the nozzles. Both non-reactive residence time distribution simulations as well as reactive steady-state simulations are used to compare the different geometries in terms of mixing and process gas homogeneity.

#### Steam cracking in the jet stirred reactor

The jet stirred reactor is part of an electrobalance setup discussed by Muños Gandarillas et al.. This setup is used to study the kinetics of coke formation during steam cracking of hydrocarbons (Muñoz Gandarillas et al., 2014a, b).. Via a complex set of reactions involving reactive radical intermediates, hydrocarbons are converted to valuable light olefins and aromatics. An inherent side reaction in steam cracking is the formation of a carbonaceous deposit on the reactor walls, referred to as coke.

The main purpose of the jet stirred reactor in the case of steam cracking is to investigate the effect of several parameters on the rate of coke formation. The parameters are usually categorized as process parameters (temperature, pressure, feed composition, feed flow rate, etc.), additives (sulfur containing molecules such as hydrogen disulfide or dimethyl disulfide) and material conditions (tube metallurgy, roughness, pretreatment with sulfur or oxygen, coatings, etc.). Coke deposition is measured using a small metal coupon, characteristic of the reactor wall, (dimensions 0.01 m x 0.008 m x 0.001 m) in the JSR, hanging form a wire connected to an electrobalance. The time evolution of the mass of the coupon is directly correlated to the deposition of coke, and hence, the rate of coke formation can be derived from the weight difference over time measured by the electrobalance.

Three possible jet stirred reactor geometries have been studied in this work differing in the orientation of the nozzles. These are displayed in Figure 2. The nozzles are oriented in a mutually perpendicular fashion in the '90°' design. The second design referred to as 'down' orients all the nozzles downwards. The third design referred to as '45°' maintains mutual perpendicularity similar to the 90° case but changes the orientation of the jets with respect to the outlet. Residence time distribution simulations and reactive simulations are performed on each of these geometries.



Figure 2. Jet stirred reactor geometries; (a)  $90^{\circ}$ , (b) down, (c)  $45^{\circ}$ .

#### **Residence time distribution analysis**

A residence time distribution (RTD) analysis provides a straightforward and low-cost method to assess the degree of macro-mixing in a reactor (Froment et al., 2010). In this case, the residence time distribution experiment has been executed in silico, using the commercial CFD package ANSYS Fluent. The main process gas component is N2 while the tracer component is CO<sub>2</sub> with a constant mass fraction at the inlet of 0.03. The outlet pressure is 101325 Pa and the inlet temperature is 900 K. All walls are adiabatic, resulting in an isothermal simulation. The Reynolds Stress Model (RSM) is used to model the effect of turbulence. A transient simulation with a time step of 5 10<sup>-6</sup> s is performed while logging the outlet mass fraction of the tracer component CO<sub>2</sub>. The full inlet and outlet are also explicitly modeled to ensure fully developed flow in the nozzles and to account for possible recirculation effects in the cylindrical outlet section respectively.

The resulting residence time distribution profile for the 90° geometry is shown in Figure 3 in the form of the derivative of the  $CO_2$  mass fraction at the reactor outlet. The expected profile is fitted against the obtained curve. As described in Froment et al., the 'tanks-in-series' model can be used to determine the amount of perfectly mixed vessels in series required to obtain the particular residence time distribution curve. The calculation is based on the variance of RTD curve as a measure for its width. The theoretical value for a perfectly mixed reactor is 1, while the theoretical value for an ideal plug flow reactor is equal to infinity. The number of tanks-in-series in this case is 2.05, which indicates a certain deviation from ideal mixing in this jet stirred reactor.



Figure 3. Derivative of the  $CO_2$  mass fraction at the outlet. ---- experimental profile, ---- fitted profile.

The most important source of non-ideality in the reactor is the incomplete recirculation of the process gas. The recirculation induced by the jets is not sufficiently strong to establish a homogenous process gas composition. A part of the process gas exits the reactor directly after being injected by the jet close to the exit. This so-called short-cut stream is visible in the sharp peak in the experimental profile (dotted line) in Figure 3 at t=0.033. Maximizing homogeneity inside a jet stirred reactor requires optimization of the nozzles' positions, that is maximizing the internal recirculation of the process gas.

#### Reactive computational fluid dynamics simulation

Reactive computational dynamics simulations of steam cracking reactors have been applied to full scale industrial reactors (Schietekat et al., 2014) and have been validated with industrial data. The simulation procedure is applied to the case of ethane cracking in the three proposed jet stirred reactor geometries.

The simulations are performed using the commercial CFD package ANSYS Fluent. Turbulence is accounted for via the ko-SST model. Enhanced wall functions are implemented to resolve near-wall effects. The chemical source terms are calculated via a reduced single-event micro-kinetic network based on the work of Pyl (Pyl, 2013). It contains 37 transported molecules and 43 radicals for which the concentrations are determined based on the pseudo steady state approximation (PSSA). The total feed flow rate is 3.88 10<sup>-5</sup> kg s<sup>-1</sup> at a temperature of 900 K. The feedstock is ethane with a steam dilution of 0.33 kg/kg. The outlet pressure is 101325 Pa. As the quartz of the reactor body is explicitly resolved, heat transfer is simulated in a conjugated way. A heat flux of 22 10<sup>3</sup> W m<sup>-2</sup> is applied to the outer surface, resulting in a total heat flux to the reactor of 116.45 W. This thermal energy is required in steady state for heating up the process gas to the appropriate temperature and for the endothermic steam cracking reactions. The most important results of the simulations are summarized in Table 1.

Table 1. Ethane cracking simulation results in three jet stirred reactor geometries; T(..) = temperature, X(..) = conversion, w(..) = dry mass fraction, P(..) = pressure.

, ( )	2		/ / /	1
		90°	down	45°
T(outlet)	Κ	1105	1110	1101
T(coupon)	Κ	1092	1106	1106
T(thermowell)	Κ	1067	1123	1107
X(reactor)	%	58.10	62.07	58.40
X(outlet)	%	64.65	69.95	66.17
w(ethene,outlet)	wt%	42.72	50.10	51.96
P(inlet,abs)	Pa	103482	103563	103502

The outlet temperatures vary within a small interval of 9 K. The two most relevant temperatures in the jet stirred reactor are the temperature measured by the thermocouple inserted in the thermowell and the surface temperature of the metal coupon. The purpose of the thermowell temperature measurement is to provide an indication of the surface temperature of the coupon as this is the temperature at which the coke is formed. Ideally, the difference between thermowell temperature and coupon temperature is small. The difference is 24 K in the 90° case, -17 K in the down case and -1 K in the  $45^{\circ}$  case, indicating that the  $45^{\circ}$  case is better in terms of temperature homogeneity.

The conversion is reported at two points, i.e. at the interface between the spherical reactor part and the cylindrical outlet part (X(reactor)) and at the end of the cylindrical outlet part (X(outlet)). The conversion after the spherical part of the reactor is similar for the 90° and 45° case and about 4 % higher for the down case, pointing to a higher average residence time in the down case. The additional conversion in the outlet part is 6.5 % in the 90° case, 7.9 % in the down case and 7.8 % in the 45° case. The total conversion in the down case is significantly higher compared to the other two cases because of a longer average residence time. The ethene yield of the down case and 45° case is 7.5 wt% and 9.0 wt% higher respectively compared to the 90° case. This higher yield is most likely explained by an increased homogeneity in the residence time and hence the absence of recirculation zones in which ethene reacts via bimolecular reactions to heavier olefins or aromatics. The pressure drop in the 45° case is 20 Pa higher compared to the 90° case while the pressure drop increases with 70 Pa in the down case compared to the 90° case. As the major part of the pressure drop occurs in the nozzles, the difference in pressure drop is only in a minor way affected by how much the mean flow direction of the entering process gas is changed when flowing through the nozzles.

#### Conclusions

The design of a jet stirred reactor for investigating kinetics of coke formation during pyrolysis or steam cracking has been designed. An *in silico* residence time distribution experiment was used as first indication of the degree of non-uniformity on the macro-mixing scale. Reactive ethane cracking simulations in three selected geometries indicate that temperature homogeneity in the  $45^{\circ}$  case is superior to the other cases.

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## AN APPROACH TO DEVELOP A KINETIC MODEL FROM A STIRRED TANK REACTOR ACCOUNTING FOR THE ROLE OF HYDRODYNAMICS: (+)-NOOTKATONE BIOCONVERSION

Carlos O. Castillo-Araiza<sup>1\*</sup>, Dulce Palmerin<sup>2</sup>, Miguel Arellano<sup>2</sup>, Arely Prado<sup>2</sup>, Abhishek Dutta<sup>3</sup> and Sergio Huerta-Ochoa<sup>2\*</sup>

<sup>1</sup> Grupo de Procesos de Transporte y Reacción en Sistemas Multifásicos. Depto. de IPH, Universidad Autónoma Metropolitana. P.A. 55-535, 09340 Iztapalapa, México D.F., México. <sup>2</sup>Departamento de Biotecnología, Universidad Autónoma Metropolitana. P.A. 55-535, 09340 Iztapalapa, México D.F., México.

<sup>3</sup> Departement Materiaalkunde, KU Leuven, Kasteelpark Arenberg 44 bus 2450, B-3001 Heverlee-Leuven, Belgium. \* To whom all correspondence should be addressed: SHO(sho@xanum.uam.mx) and C.O.C.A (coca@xanum.uam.mx)

#### Abstract

In this work an extrinsic kinetic model for (+)-valencene oxidation to (+)-nootkatone is developed. The kinetic study is conducted in a batch stirred tank reactor (BSTR) containing a pseudo aqueous phase, (+)-valencene and Yarrowia lipolytica, and a gas phase to feed the oxygen necessary for the bioconversion. Firstly, the role of hydrodynamics on mass transport in absence of bioconversion is assessed. Particularly, velocity field from the gas phase and aqueous phases is determined using computation fluid dynamics (CFD) in general, and  $\kappa$ - $\epsilon$  turbulence model bubble model, respectively, in particular. Thus, hydrodynamics from both aqueous and gas phase in the BSTR is coupled to the oxygen mass transport model accounting for convective, dispersive and interfacial phenomena. From this end, local interfacial mass transport coefficients are determined, and are integrated to obtain the corresponding effective oxygen mass transport coefficient ( $K_L a$ ) that accounts for the role of hydrodynamics on mass transport in some detail. Secondly, this information is transferred to the averaged BSTR model that couples oxygen mass transport from the gas to the pseudo aqueous phase to kinetics. The reaction mechanism proposed follows the Langmuir-Hinshelwood formalism and considers the loss of cell viability as a deactivation mechanism affecting bioconversion. Approximations of the pseudo equilibrium of reaction rates or steady state intermediary species are not considered, thus, an analysis of the role of each reaction step involved in the bioconversion is accounted for. The BSTR model and proposed methodology adequately describes the observations with and without bioconversion. The regression and the estimated parameters are statistically significant, which lead to carry out a reliable analysis for understanding the kinetic behavior of Yarrowia lipolytica and how it is limited by oxygen mass transfer from the gas phase to liquid phase.

Keywords: Hydrodynamics, Kinetics, Stirred Tank Reactor, (+)-Nootkatone Bioconversion

#### Introduction

Batch stirred tank reactor (BSTR) is widely used to carry out multiphase bioconversion (Gas-Liquid-Solid) aimed to produce fine chemicals of economic importance for pharmaceutics, fragrance and industries. Bioconversions using aerobic food microorganisms need from substrates contained in aqueous phase and from gas phase to produce the desired chemical via the corresponding metabolic processes. Nevertheless, the substrate supplied from gas phase, i.e., oxygen, might affect negatively the bioconversion performance because of its scarcity in aqueous phase and, hence, in biocatalyst [Y. S. Liu et al., 2006]. This limited concentration of substrate in aqueous phase is mainly related to its poor transport from gas to aqueous phase [A. Karimi et al., 2011]. From this end, oxygen transfer rate from gas to aqueous phase is normally characterized through the proper determination of the mass transport coefficient  $(K_La)$ .  $K_La$  along with the kinetic parameters is the most important parameter implied on the design and operation of mixing-sparging BSTR.

The oxygen mass transport coefficient is experimentally obtained using the dynamic method, which allows to evaluate the oxygen mass transfer rate [A. Karimi *et al.*, 2011]. The  $K_La$  is normally estimated using the average transport equation, wherein oxygen concentration is dependent of time but independent of bioreactor position [D. Cascaval et al., 2011]. The  $K_{La}$ values obtained are generally used to develop correlations. However, there are uncertainties related to the values obtained from these correlations, mainly owed to the strong influence of bioreactor geometry and operating conditions used to developed such correlations [Montes et al., 1999]. The main lack on the determination of  $K_L a$ , is that the aforementioned approach neglects the role of local velocities of gas and liquid phases on oxygen mass transport rate in the BSTR. In this regard, studies based on Computation Fluid Dynamics (CFD) have accounted for the role of hydrodynamics on oxygen mass transport, allowing to have a better understanding and visualization of the distribution of the liquid and gas velocities and oxygen mass transfer rate in the BSTR [Kerdouss et al., 2008]. Nevertheless, constrains in computing time have no allowed to study the effect of hydrodynamics on oxygen mass transport in presence of biorreaction and, hence, during the developing of a kinetic model wherein parameter estimation is necessary.

Studies from the research group [D. Palmerin-Carreño *et al.*, 2015] identified to the multiphase partitioning bioreactor conception as a potential technology to enhance the productivity of (+)-nootkatone from the oxidation of (+)-valencene

contained in orange essential oil using a biological process. Nevertheless, during the design of this bioreactor concept, the productivity of (+)-nootkatone, as observed in the production of other sesquiterpenes in a multi-phase system, can be limited by low mass transfer rates at interfaces (gas-liquid or liquid-liquid) [A. Karimi *et al.*, 2011]. In this respect, basic engineering related to the design of this bioreactor concept requires from independent studies of oxygen mass transport with and in absence of biorreaction in order to have a successful scaling-up.

The aim of this work is to determine the role of oxygen mass transport in a Liquid-Gas BSTR. The study is conducted in 1000 ml bioreactor containing a pseudo aqueous phase, (+)-valencene and Yarrowia lipolytica, and a gas phase to feed the oxygen necessary for the bioconversion. Particularly, the role of hydrodynamics on oxygen mass transport in absence of bioconversion is assessed, then, this information is transferred to develop an extrinsic kinetic model for (+)-valencene oxidation to (+)-nootkatone on *Yarrowia lipolytica* whose loss of viability cellular is determined and accounted for.

#### PROCEDURES

#### **Experimental system**

A batch stirred tank reactor (BSTR), model ADI 1025, Applikon of 10000 ml was used for experiments with and in absence of bioconversion. The bioreactor had an inside diameter  $D_T = 9.5$  cm and an operation volume of 700ml (H<sub>L</sub>=9.12 cm. The bioreactor was equipped with a single Rushton turbine with 6 paddles, with a diameter  $D_i = 4.53$  cm, located 4.53 cm from the base of the container. The bioreactor had 2 equidistant deflectors of 1.0 cm in width to improve mixing.

#### Mass transfer experiments

Experiments to calculate the overall oxygen mass transfer coefficients,  $K_La$ , were carried out according to the dynamic method. Optical fiber for Dissolved Oxygen (DO), mini sensors (PreSens, GmbH Germany) were used for  $K_La$  determination. A factorial design  $3^2$  was considered to. The response was the dissolved oxygen concentration whereas the two experimental variables were the revolutions per minute (rpm: 200- 400) and the air flow rate in terms of volume of air per volume of medium per minute (vvm: 0.5-1).

#### **Kinetic experiments**

Yarrowia lipolytica was previously selected for its capability to convert (+)-valencene to (+)nootkatone from a screening among 6 selected strains (fungi and yeasts). Y. lipolytica was isolated from copra meal that was provided by the Laboratory of Bio-Process of the University of Guadalajara (U de G), Mexico. Yeast growth and bioconversion were maintained at 200 rpm. Temperature was maintained at 30°C. The pH was monitored using an AppLiSens Z001023511 pH electrode (Applikon) and controlled at 5.5 using 2 M HCl.. The air flow rate in the bioreactor for yeast growth and bioconversion was fed through a perforated "L" tube with seven holes of 1.0 mm in diameter. A refrigerant was located at the air exit to avoid sesquiterpenes evaporation from the bioreactor. Bioconversion studies were conducted after the growth phase of Y. lipolytica (33 h), by adding a concentrated solution of (+)-valencene to reach a final concentration of 1500 mg L<sup>-1</sup>. An experimental design varying oxygen (0.5-2 vvm), (+)-valencene (1500-35003500  $mgL^{-1}$ ) and (+)-nootkatone (0-600) $mgL^{-1}$ ) concentration was carried out. During experiments, the loss of cell viability was determined by measuring the concentration of living cells using the methodology described by Bonora and Mares. For the sake of brevity details on all experimental methodology are not presented but can be consulted [D. Palmerin-Carreño et al., 2015].

#### **Oxygen Mass transfer model**

Overall oxygen mass transfer coefficient,  $K_L a$  was evaluated through two approaches. The conventional one, which makes use of an average transport equation given as follows (hereafter will be named as CA):

$$\frac{dC_{o_2}}{dt} = K_L a \left( C_{o_2}^{*} - C_{o_2} \right)$$
(1)

Where  $C_{O_2}^{*}$  and  $C_{O_2}^{*}$  are the oxygen concentrations at equilibrium and in the aqueous phase, respectively. The second approach makes use of computation fluid dynamics (CFD). Thus,  $\kappa$ - $\epsilon$  turbulence model and bubble model are used to describe the hydrodynamic from both liquid and gas phases, respectively. Then, hydrodynamics in the BSTR is coupled to the oxygen mass transport model accounting for convective, dispersive and interfacial (Gas-Liquid) mass transport phenomena. These simulations allow to calculate the local interfacial mass transport coefficients, which are used to obtain the corresponding effective  $K_L a$  that so far accounts for the role of hydrodynamics on mass transport in some detail. The calculation of KLa using CFD hereafter will be named as CFD-A. Because of space constraints, in the following lines the average mass transport model, describing oxygen concentration profiles in the liquid phase, is the only one presented.

$$\frac{dC_{o_2}}{dt} + \overline{U_L} \cdot \nabla C_{o_2} = M_{G-L} + \nabla \cdot \left( -\overline{D} \nabla C_{o_2} \right)$$
(2)

$$M_{G-L} = K_L a \left( C_{O_2} * - C_{O_2} \right)$$
(3)

$$K_{L}a = \alpha \left[ (4nn)^{1/3} (3\varphi_{G})^{2/3} \frac{(\rho_{G} - \rho_{L})}{U_{T}^{2}} (\overline{U}_{G} - \overline{U}_{L}) \right]$$
(4)

where  $\overline{U}_{L}$  is the velocity vector, determined by  $\kappa$ - $\varepsilon$  turbulence model,  $\overline{D}$  is the dispersion tensor, and  $M_{G-L}$  takes into account the mass transport of oxygen from gas to liquid phase.

#### **Kinetic model**

The reaction scheme for the bioconversion of (+)-valence to produce (+)-nootkatone accounts for an intermediate produced from the former and used to produce the latter. This intermediate is identified as (+)-nootkatol. Figure 1 displays the reaction mechanism proposed in the current study, which is based on the Langmuir-Hinshelwood-Hougen-Watson formalism, considering only one type of enzymes/active sites (CYP 450) to produce (+)-nootkatone out of (+)-valence.



Figure 1. Reaction mechanism based on LHHW formalism. E: enzyme; I:(+)-nootkatol; P: (+)-nootkatone;  $O_2$ : oxygen; and  $k_i$ s: kinetic constants.

The main aspects of the mechanism along with the relevant rate equations are listed below:

(a) Oxygen enters the bioconversion cycle generating a sufficient amount of enzyme-oxygen (EO) complex.

$$\mathbf{r}_{1} = \mathbf{k}_{1} N_{T} \boldsymbol{\theta}_{E} \mathbf{C}_{\mathbf{0}_{2}} + \mathbf{k}_{-1} N_{T} \boldsymbol{\theta}_{E\mathbf{0}}$$
(5)

(b) EO complex reacts with the substrate (+)-valencene and forms an enzyme-oxygen-substrate (EOS) complex.

$$\boldsymbol{r}_{2} = \boldsymbol{k}_{2} \boldsymbol{N}_{T} \boldsymbol{\theta}_{EO} \boldsymbol{C}_{S} - \boldsymbol{k}_{-2} \boldsymbol{N}_{T} \boldsymbol{\theta}_{EOS}$$
(6)

(c) The EOS complex is converted into an enzymeintermediary (EI) complex; the intermediary being (+)nootkatol.

$$I_{3} = k_{3}N_{T}\theta_{EOS} - k_{-3}N_{T}\theta_{EI}$$
(7)  
(d) The intermediant detaches from the ensure thus

(d) The intermediary detaches from the enzyme, thus, the intermediary is formed.

$$\boldsymbol{r}_{4} = \boldsymbol{k}_{4} \boldsymbol{N}_{T} \boldsymbol{\theta}_{EI} \tag{8}$$

(e) The EI complex is converted to an enzyme-product ((+)-nootkatone) (EP) complex.

$$r_{5} = k_{5} N_{T} \theta_{EI} - k_{-5} N_{T} \theta_{EP}$$
(9)

(f) The EP complex is detached and product, (+)-nootkatone is produced.

$$r_6 = k_6 N_T \theta_{EP} \tag{10}$$

Components adsorbed on active sites are described as follows:

$$N_{\tau} \frac{d\theta_{EO}}{dt} = 2r_1 - r_2 \tag{11}$$

$$N_{\tau} \frac{d\theta_{EI}}{dt} = r_3 - r_4 - r_5 \tag{12}$$

$$N_{\tau} \frac{d\theta_{EP}}{dt} = r_5 - r_6 \tag{13}$$

$$N_{\tau} \frac{d\theta_{E}}{dt} = -2r_{1} + r_{4} + r_{6}$$
(14)

$$N_{\tau} \frac{d\theta_{EOS}}{dt} = r_2 - r_3 \tag{15}$$

$$N_{\tau} = N_{\tau_0} \theta_x \tag{16}$$

The Generalized Power Law Expression is used to describe the cell deactivation.

$$\frac{d\theta_x}{dt} = -k_{in}([\theta_x - \theta_{ss}])^n \tag{17}$$

#### **Reactor model**

The reactor model accounts for the following assumptions: (a) The reaction system is operated isothermally; (b) There is neither evaporation of the substrate nor of the product; (c) The cells do not encounter any shear damage due to stirring in the bioreactor; and (d) The aqueous phase and the microorganism are considered as a pseudo homogenous phase. Thus, the reactor model is a pseudo-heterogeneous one that takes into account gas and pseudo liquid phases. The oxygen transport from the gas phase to the pseudo aqueous phase is described by the following equation:

$$\varepsilon_a \quad \frac{dCO_2}{dt} = \varepsilon_g K_L a (CO_2 * - CO_2) \pm R_{O_2} \tag{18}$$

In this model two sets of  $K_La$  are evaluated. One set comes from CA and the other set of  $K_La$  comes from CFDA. The substrate (S), (+)-valencene, the product (P), (+)-nootkatone and the intermediary (I), (+)-nootkatol, are only considered in the pseudo aqueous phase as follows:

$$\varepsilon_a \quad \frac{d[i]_a}{dt} = R_{i_a}; i = S, P, I \tag{19}$$

The estimation of the kinetic parameters makes use of the weighted least squares of the residuals (RSS) following the next objective function:

$$RSS(b) = \sum_{j}^{n_{exp}} \sum_{k}^{n_{rep}} W_{jk} (y_{ij} - \hat{y}_{ij}) (y_{ik} - \hat{y}_{ik})$$
(20)

The kinetic parameters are estimated by a software program (ODRPACK 2.01) using multi-response nonlinear regression using Levenberg-Marquardt algorithm with 95% confidence interval. To determine the statistical significance of these parameters the t-test is used, while the F-test is used to obtain the regression significance.

#### Results

Figure 1 presents oxygen mass transfer results in absence of biorreaction. Figure 1 displays a comparison between observed and predicted dissolved oxygen concentration as a function of time. Predictions are obtained on the basis of CFDA using Comsol Multiphysics 5.0. For the sake of brevity, results at two different operating conditions are only presented herein, i.e., 200 rpm and 0.5 vvm; and 200 rpm and 1vvm. Aside, Concentration profiles and averaged values of  $K_{La}$  obtained by CA and by CFDA, indicate how oxygen mass transfer rate is improved at higher vvm. Nevertheless,  $K_{La}$  values obtained by CFDA are from ca. 20 to 40 times smaller than those  $K_{La}$  values obtained by CA. Hydrodynamics due to its negative effect on oxygen mass transport, considered in the CFDA, seems to be the main phenomena leading to the lower averaged values of *KLa*. The negative effect of hydrodynamics on mass transfer in BSTR has also been identified from experimental studies using image analysis techniques [G. Corkidi *et al.* 2012]



Figure 2. Comparison between observed dissolved oxygen concentration and that predicted by CFD at two operating conditions. BSTR figure shows velocity field of liquid phase at 200 rpm and 1 vvm. KLa (200 rpm and 0.5 vvm) is equal to ca.  $0.21h^{-1}$  by CFDA and ca.  $8.0 h^{-1}$  by CA. Besides KLa (200 rpm and 1 vvm) is equal to ca  $0.56h^{-1}$  by CFDA and ca  $12.26 h^{-1}$  for CA.



Figure 3. Comparison between concentration profiles observed and those obtained by model using either the  $K_{La}$ determined from CA or CFDA. Symbols are observations; dashed lines are model fitting using KLa from CA; and continuous lines are model fitting using  $K_{La}$  from CFDA.

Figure 3 displays a comparison among observed concentration profiles under reaction conditions and those fittings using  $K_La$  values obtained via either CFDA or CA. Both sets of  $K_La$  lead to regression and parameters statically significant. Nevertheless, when  $K_La$  values obtained via CA are evaluated, kinetics is not bale to describe observations. The larger value of  $K_La$  gives rise to a an outstanding oxygen mass transport between gas and liquid phases, which in turn leads to an overproduction of (+)- nootkatone out of (+)-valence. This model performance is related to to an over formation of the enzyme-oxygen complex (0.015)

compared to that one (0.236) obtained when the  $K_La$  value acquired via CFDA is used to develop the kinetics. Besides, adequate predictions of dissolved oxygen concentration seem to be another important criteria to evaluate the sets of  $K_La$  values obtained by either CFDA or CA. In this regard,  $K_La$  determined via CFDA is able to describe oxygen observations, so far, capturing those transport resistances between gasliquid phases.

#### Conclusions

Oxygen mass transfer rate is normally characterized through the determination of the  $K_L a$ from laboratory experiments. Nevertheless, its determination by the CA that makes uses of average transport equation neglecting hydrodynamics seems to lead to inadequate predictions under reaction conditions. In this regard, hydrodynamics, namely local velocities of gas and liquid phases in the BSTR seem to affect negatively oxygen mass transport. In this sense, CFDA gives rise to lower values of  $K_L a$ , which in turn are able to describe observations with and in absence of reaction. The proposed approach allows to quantify the role of hydrodynamics on oxygen mass transport through the proper determination of the effective parameter,  $K_{La}$ . Besides, the use of this parameters in the averaged reactor model allows to develop in too much less computing time a kinetic model, wherein parameter estimation is necessary.

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## DETAILED MICROKINETICS AND THE MATHEMATICS OF DIFFUSION AND SHAPE SELECTIVE CATALYSIS

Fei Wang, Yuxin Li, Usman Muhammad, Dezheng Wang<sup>\*</sup>, and Yao Wang Department of Chemical Engineering, Tsinghua University Beijing, 100084 China Email: wangdezheng@tsinghua.edu.cn

*Abstract* When detailed chemistry microkinetics is used as the chemical kinetics in a zeolite, zeolite activity and shape selectivity are obtained by solving the diffusion-reaction equations inside the zeolite to provide the source term in the reactor continuity equation. This requires further getting the diffusion coefficients of the reacting molecules in the zeolite. Numerical modeling of the sorption kinetics method is suggested for measuring the diffusivity of a molecule in a zeolite.

Keywords Diffusion Limitation, Shape Selectivity, Microkinetics.

#### Introduction

Industrial gas-solid catalyzed reactions occur with the gases diffusing inside a porous solid. In zeolite catalysts, the diffusion rates are usually slow enough that the coupling between diffusion and reaction, which causes diffusion limitation and shape selectivity, must be taken into account. In another aspect, the treatment of chemical kinetics by detailed chemistry microkinetics (DCMK) is becoming preferred because DCMK gives mechanistic insight into the reactions. However, at present there is no discussion of how to treat diffusionreaction coupling when DCMK is used.

The mathematics of diffusion-reaction coupling as treated in textbooks, i.e., using the Thiele modulus or Damköhler number, is not compatible with DCMK because it assumes a rate controlling step (RCS). With a RCS, all chemical species react at the same rate, which allows using an overall rate expression that comprises only the concentration of one gas species, and the diffusion-reaction coupling needs only the diffusion rate of that gas. In contrast, DCMK is used to obviate a RCS simplification when the RCS use is not valid, so with DCMK, different chemical species react at different rates. Due to this, the mathematics comprise a set of species continuity equations, one for each species. These are the CFD equations, which are simple for a laboratory reactor because turbulence and the pressure drop (momentum equations) can be ignored, and often the energy equations can be too. However, the source term is complicated and in the computer program, this would be a functor of the diffusion-reaction equations that describes what happens inside the zeolite. Although solving the equations is computationally demanding, it is now possible with a multi-core PC because the computation is easily parallelized. The problem now is the diffusion-reaction equation for each adsorbate in the

zeolite contains a diffusion coefficient. Thus, handling diffusion-reaction coupling when DCMK is used needs the solving of the problem of getting the many needed diffusion coefficients.

Here, we report an experimental method to measure the diffusivity of a molecule in a zeolite which is a simple modification of the sorption kinetics method. It gives the diffusivity from the data collected in the measurement of the adsorption isotherm of the gas, which means it needs neither a special instrument nor measurement procedure for the diffusivity. The diffusion coefficients of all the gases are available from the measurement of their adsorption isotherm. In addition, it also gives the data of how the diffusivity changes versus the surface concentration. The method works by adding the use of numerical analysis to the sorption kinetics method, which has been reviewed in Karger, Ruthven and Theodorou (2012). In the conventional sorption kinetics method, a special instrument is required because the method uses the analytic solution of the diffusion equation to get the diffusivity. However, an analytic solution is only available when the boundary condition at the outer surface is that the gas phase pressure (concentration) there is constant. Since it is this boundary condition that requires the use of a special instrument, we can avoid this by changing the boundary condition to use a changing gas pressure in the gas around the zeolite, which was already accurately measured versus time in an isotherm measurement. To use this method, we only need to add a numerical algorithm that solves the diffusion equation of the gas in the zeolite for a variable pressure boundary condition at its outer surface.

#### Experimental

The catalyst used was a SAPO-34 zeolite described in Li et al. (2014). Its surface area, pore volume and pore size were, respectively, 1247 m<sup>2</sup>/g, 0.297 cc/g and 0.552 nm. The particle sizes were 1 to 2  $\mu$ m. The acid site

<sup>•</sup> To whom correspondence should be addressed

density was calculated from SEM-EDS and NH<sub>3</sub>-TPD data to be 1.0 mml/g.

The measurement of an adsorption isotherm was performed using an adsorption volumetric manometry apparatus that has been described in Kobayashi et al. (2014). The adsorbates were methanol, dimethyl ether (DME), ethene, propene, methane and propane. Our interest in this system is for the MTO process. Adsorption was carried out after the sample was preheated at 400 °C for 5 hours under vacuum, then first saturated by the gas to cover the sites of irreversible adsorption and evacuated so that the subsequent measurement measured only the reversibly adsorbed gas. Equilibrium in the gas phase was verified before admitting the next dose by there being no change in the gas pressure. Equilibrium was usually established within two hour after each dose for an alkane and within 30 min for the other gases.

Each dose, which would give a point on the adsorption isotherm, also comprised the data used to extract the diffusivity. Modifications were made to the data collection to use a fast A/D board in order to ensure these data had good time resolution, which was unimportant for measuring an adsorption isotherm but was important for measuring diffusivity. Also, the gas should be dosed in quickly to avoid losing too much data for the first diffusion stage, but the dosing should be steady to avoid any surge in pressure in the sample cell, which could take time to decay and would cause loss of data for the early diffusion stage. The novel feature with respect to measuring the diffusivity was that the pressure of the gas surrounding the porous powder was allowed to decrease naturally due to gas diffusion into the porous powder until equilibration was reached, that is, this method obviates the need to make provisions to maintain a constant pressure in the sample cell. The principle of the measurement was the use of mathematical modeling, popularly known as "curve fitting", to extract the diffusivity from the pressure versus time curve (uptake curve) of the sample cell.

#### **Results and Discussion**

Microscopic methods for measuring gas diffusivity in a zeolite, e.g., tracing the random walk of a molecule by NMR or microscopy, are not suitable for general use, and so we considered a macroscopic method based on sorption kinetics. Previously, a relaxation method, which is usually a step response method where a step change from  $P_0$  to  $P_\infty$  is made in the gas pressure, is used and the curve of the concentration of the gas in the porous powder versus time (called the soption or uptake curve) is measured as the system relaxes to its new equilibrium state. Most experimental techniques measure the uptake curve by using a highly sensitive microbalance to measure the change in the weight of the powder versus time. However, this is disadvantageous because these microbalances are very expensive, and so there is an incentive to instead measure some change in the gas surrounding the powder versus time as the

response curve from which the uptake curve can be deduced. One idea in the literature was to use the gas replenishment rate but this is not easy because the gas uptake by the zeolite is very tiny compared to experimentally-easily-measured flow rates. Our idea is that the pressure change itself contains the data for the diffusion rate, which can be used by adding an auxiliary equation of the mass balance for the sample cell,

$$\frac{dN}{dt} = -x \cdot m_{cat} + F \tag{1}$$

*t* is the time variable, *x* is the molar flux of diffusing gas into the zeolite per gram sample and is a function of time, that is, it is x(t), and *F* is the experimentally controlled dosing of the gas, expressed as the molar flow of gas into the sample cell. This is also a function of time, that is, it is F(t). x(t) is calculated from the solution of the diffusion equation in the zeolite,

$$\frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 D_r \frac{\partial q}{\partial r})$$
(2)

The boundary conditions for Eq. (2) are

$$t < 0, \quad P = P_0, \quad q = q_0(\forall r) \tag{3a}$$

$$t \ge 0$$
,  $P = P(t)$ ,  $q(t)\Big|_{r=R} = q_R^n$ ,  $\frac{\partial q}{\partial r}\Big|_{r=0} = 0$  (3b)

$$q_0 = f(P_0), \quad q_R^{\ n} = f(P)$$
 (3c)

The conditions in Eq. (3a) and at r=R in Eq. (3b) assume gas-adsorbate equilibrium, that is,  $q_0 = f(P_0)$ ,  $q_R^n = f(P)$ , where *f* is the measured adsorption isotherm function. Eq. (2) is written for a sphere, but other geometries may be used depending on the sample. x(t) is calculated from the solution of Eq. (2) by computing the flux into the zeolite,

$$x(t) = \frac{4\pi R^2}{\frac{4}{3}\pi R^3} \rho \left. D_R \frac{\partial q}{\partial r} \right|_{r=R} = \frac{3\rho}{R} \left. D_R \frac{\partial q}{\partial r} \right|_{r=R}$$
(4)

T

F(t) in Eq. (1) was calculated per unit time step from experimental measurement of the pressure change in the container supplying the gas dose by

$$F_{i-1} \cdot \Delta t = \Delta F_{i-1} = \frac{(dP_i - dP_{i-1})V_1}{RT_1}$$
(5)

The times of the measured values of dP recorded in the computer did not match exactly with the discretized time steps. An interpolation technique was used to get the values at the required discretized times using the measured  $dP(t) \sim t$  curve.

With present personal computers, very small steps can be taken so that Euler's method is adequate for solving Eq. (1). The Crank-Nicholson method was used for solving Eq. (2). From Eq. (1), the number of moles of gas in the sample cell was obtained as a function of time. The ideal gas law was used to convert this curve to



Figure 1. Measured and fitted uptake curves for propane diffusion and adsorption in SAPO-34.

pressure units to give the  $P(t) \sim t$  curve, which was the simulated uptake curve. The diffusion coefficient parameter was optimized to get the best fit of this with the measured uptake curves.

Figure 1 shows an example of this fitting with data from propane diffusion and adsorption in SAPO-34. The diffusion coefficient parameter that gave the best fit simulated uptake was  $0.7 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}$ . Figure 2 shows an example of data from propene diffusion and adsorption in SAPO-34. The fitted diffusion coefficient for propene in SAPO-34 was  $2.0 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ . It can be noted that the experimental curve in figure 2 does not become horizontal but kept decreasing. This was due to that propene was already reacting although the measurement was made at the low temperature of room temperature. The propene data also indicated that this



Figure 2. Measured and fitted uptake curves for propene diffusion and adsorption in SAPO-34.

method of measurement can measure a fastest diffusivity of  $5.0 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ , where the uptake curve would have to be measured within 10 s.

Unfortunately, there are no good data on these diffusivities in the literature that can be used to check on the accuracy of the measurement. Qualitatively, the quite different time scale of the time axis in figures 1 and 2 reflected that the diffusion rates for the two different molecules were very different, and the order of the scale on which they differed, that is, 300-fold, was reasonable. However, the magnitudes for the diffusivities reported above would be considered quite low compared to values typically used in the literature, but conversely, we could also view the values used in the literature as disposed to the high side.

Unfortunately, we can only make a qualitative comparison and with a different zeolite at that because much more data are available for ZSM-5, while data for SAPO-34 are scarce. Hansen et al. (2009) in a detailed kinetics analysis of diffusion in H-ZSM-5 gave a value of  $2 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$  for benzene in ZSM-5. In consideration of the relationship of the size of benzene to the ZSM-5 channels and of propene to the SAPO-34 pore network, and their diffusion limitation behavior, we could expect their diffusivity to be about the same. In terms of the magnitude of the number, our value for the diffusivity of propene in SAPO-34 was one order of magnitude less than that of benzene in ZSM-5. This may be due to that Hansen et al. considered the zero loading diffusivity. In our measurements, we have observed that the diffusivity was quite sensitive to whether there was no or some adsorbate in the zeolite, and this difference can lead to a difference of ten-fold in the diffusivity. We comment here that in our measurement method, it is easy to measure diffusivity versus adsorbate concentration since the gas dosage can be chosen to be quite small.

Further points of discussion that can be interesting are in a comparison of the approach we take and that of Hansen et al. for the analysis of diffusion limitation. One difference is in how to get the diffusion coefficients. They used a simulation approach using molecular dynamics. We used an empirical approach. While we admit that much work remains to be done by us to attest the accuracy of the measurement, we feel that the same can be said about the simulation approach. The attraction of our method is that the data are already available from the measurement of the adsorption isotherm, but the method is also limited to very slow diffusion systems.

Another point that needs to be discussed is how to use the diffusivity data. Hansen et al. used the Maxwell-Stefan equations approach, which has been reviewed by Krishna (2014) who has also given the reasons why this approach is needed. We think that a Fick's law formulation may be adequate for the diffusion equation, but this is basically an opinion.

A further point is about the kind of chemical kinetics to use. Hansen et al. used a macroscopic kinetics approach, although one that is more detailed than

Langmuir-Hinshelwood kinetics. Our interest is also in the shape selectivity of the zeolite. Present treatment of zeolite shape selectivity uses the kinetic diameter of the diffusing gases compared with the pore diameter. This is an on-off selectivity prediction that does not use chemical kinetics, that is, a gas phase product is either formed or it is not. Here, we suggest using DCMK information for quantitative shape selectivity analysis to go beyond this because we have the mathematics to get diffusion-limited rates, which is true when the diffusionreaction equations inside the zeolite are used to supply the source term in the reactor continuity equation. The computation problem of this can be solved with a multicore personal computer because when these equations are solved with the method of lines and the resulting ordinary differential equations are solved with the stiff equation program given in Press et al. (2007), the program is easy to parallelize. However, the use of DCMK also has the problem of how to prune down the number of rate parameters that have to be fitted, which is a problem that has received valuable contributions from Gent University.

#### Conclusion

Diffusion coefficients of adsorbates diffusing in SAPO-34 were obtained using data from the measurement of the gas adsorption isotherm by curve fitting the pressure versus time curve of the sample cell pressure. Diffusivities less than  $5.0 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$  can be obtained. The availability of these diffusivities would enable the use of detailed chemistry microkinetics for the reaction kinetics of reactions occurring in a zeolite.

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## CFD-based design of 3D pyrolysis reactors

David J. Van Cauwenberge<sup>1</sup>, Jens Floré<sup>2</sup>, Kevin M. Van Geem<sup>1</sup>, Guy B. Marin<sup>1</sup> <sup>1</sup> Laboratory for Chemical Technology, Technologiepark 914, 9052 Ghent, Belgium, Kevin.VanGeem@UGent.be

<sup>2</sup> BASF Antwerpen N.V., Haven 725, Scheldelaan 600 B-2040 Antwerp, Belgium

#### Keywords

#### Computation Fluid Dynamics, pyrolysis, turbulence modeling, Large Eddy Simulation, OpenFOAM

Pyrolysis is the main process for the production of many valuable organic building block chemicals such as ethylene, propylene and vinyl chloride. The free-radical gas phase reactions are accompanied by secondary reactions leading to the formation of a carbonaceous coke layer on the inner walls of the reactor tubes [1]. This layer leads to an increased pressure drop over the reactor causing a loss in selectivity. Additionally, the insulating effect of the layer forces a higher furnace firing rate and higher tube metal temperatures to maintain the same conversion. In industrial plants regular decoking procedures are hence inevitable.

Because of this detrimental effect on the overall economics, the design of novel reactor geometries exhibiting reduced metal temperatures with the aim of increasing run lengths has received quite some attention [1]. In order to provide a detailed evaluation of these geometries however, one must account for the chemical kinetics, as well as the complex flow phenomena in the reactor. While reliable kinetic models with thousands of reactions and hundreds of intermediates are widely applied, implementing these efficiently in a Computational Fluid Dynamics (CFD) code remains a challenge [2]. Commercial packages such as ANSYS Fluent for example do not even allow kinetic models with more than 50 species.



Figure 1: Streamwise periodic temperature field for a spirally corrugated pipe.

In the present contribution, a variety of tubular reactor geometries were simulated using the opensource CFD code OpenFOAM. Detailed kinetics were incorporated by reduction of a hexane pyrolysis reaction mechanism, automatically generated with Genesys [3]. Turbulence modeling is achieved by application of a Large Eddy Simulation (LES) methodology, allowing the evaluation of turbulence-chemistry interaction on a much smaller scale than the commonly applied Reynoldsaveraged Navier-Stokes (RANS) models.

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## NUMERICAL SIMULATIONS OF STEAM CRACKING TEST FURNACE USING DETAILED COMBUSTION MECHANISM FOR CO AND NO<sub>X</sub> EMISSION

Yu Zhang<sup>1,3</sup>, Carl M. Schietekat<sup>1</sup>, David J. Van Cauwenberge<sup>1</sup>, Pieter A. Reyniers<sup>1</sup>, Kevin M. Van Geem<sup>1,\*</sup>, Mike Henneke<sup>2</sup>, Feng Qian<sup>3,\*</sup>, and Guy B. Marin<sup>1</sup>

 <sup>1</sup>Ghent University, Laboratory for Chemical Technology, Technologiepark 914, 9052 Gent, Belgium
 <sup>2</sup>John Zink Hamworthy Combustion, 11920 East Apache, Tulsa, OK 74116, United States
 <sup>3</sup>Key Laboratory of Advanced Control and Optimization for Chemical Processes of Ministry of Education, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China

#### Abstract

Three-dimensional steady-state computational fluid dynamics (CFD) simulations were performed in a John Zink Hamworthy Combustion test furnace intended for burner designingand evaluation . The k- $\omega$  SST turbulence model employed in the furnace simulation was validated by the experimental data of a non-reacting round jet of propane into co-flowing air from Sandia National Laboratories. A 17-step methane combustion mechanism, which is reduced from the detailed GRI-Mech 3.0 based on quasi steady state approximation (QSSA), was implemented to predict CO and NOx emission. Flue gas non-gray radiative properties were also taken into account by solving radiative transfer equations for 6 H<sub>2</sub>O and CO<sub>2</sub> absorption bands. The influence on flue gas temperature as well as NO<sub>x</sub> emissions was compared.

#### Keywords

Steam cracking, Computational fluid dynamics, Reduced combustion kinetics, NOx emission

#### Introduction

Steam cracking of hydrocarbons is the most important petrochemical process for light olefins production. The strongly endothermic cracking reactions and the high process gas temperatures in the reactor coils make that an enormous amount of heat needs to be transferred by radiation. To reduce local hot spots on the reactor walls, and consequently severe coking and material deterioration, ideally a uniform heat flux is provided to the reactor coils to extend their runlength. This led to the usage of multiple radiant wall burners in which combustion of premixed fuel and air creating small but intense flames with temperatures up to 2200 K (Baukal, 2001). However, using a large number of wall burners in a furnace always requires high maintenance and operation costs. Thus floor burners where fuel and air enter separately (with staged fuel inlet) are currently preferred over wall burners as they produce large diffusion flames. These can be as high as 4-6 meters and supply most or even all the heat needed for the cracking reactions. The latter implies that only a few burners are needed to operate the furnace.

F. Qian at fqian@ecust.edu.cn

Furthermore, raising environmental concerns and a stricter legislation have driven the design of burners to minimize NOx emissions. The latter has also prompted the use of floor burners due to their lower flame temperature. To comply with the emission regulations a lot of effort has gone to the design of ultra-low NOx burners. The performance of a new design requires intense testing in a test furnace. However, the extreme conditions in these furnaces make it difficult to obtain in-flame information such as temperature and species concentrations. The latter are needed to improve understanding of the flame behavior. To overcome these issues a numerical model accounts for the interaction between turbulence, radiative heat transfer as well as detailed combustion mechanism is extremely valuable.

In the present work a John Zink Hamworthy Combustion test furnace was simulated using a steadystate Computational Fluid Dynamics (CFD) approach. A 2D simulation of non-reacting round jet of propane into co-flowing air was performed and compared with the experimental data obtained from Sandia National Laboratories for the validation of turbulence model. For combustion modeling, an augmented reduced mechanism based on GRI-Mech 3.0 was used (Lu et al., 2008). This mechanism, consisting of 21 species and 17 lumped reaction steps, was shown to be able to satisfactorily describe steady burning of both premixed

Correspondence concerning this article should be addressed to:

K. M. Van Geem at Kevin.VanGeem@UGent.be

and non-premixed flames with extensive parametric variations. Due to the wide applicability and lower computational cost it was implemented in the current furnace simulation to account for  $NO_x$  emission. The CFD code also takes non-gray radiative properties of the flue gas into account by solving radiative transfer equations for 6 H<sub>2</sub>O and CO<sub>2</sub> absorption bands. This remedies the underprediction of flame temperature by the gray gas radiation model (Stefanidis et al., 2007; Zhang et al., 2015), which may also have effects on  $NO_x$  emissions.

#### Non-reacting round jet flow

In a long flame burner fuel enters the furnace as high velocity jet through the burner nozzle and is then mixed with co-flowing air, leading to a non-premixed diffusion flame. This requires a validated turbulence model that is able to capture the turbulence characteristics. Therefore the non-reacting mixing propane-jet flow was simulated, which has been experimentally investigated by Sandia National Laboratories (Schefer et al., 1987).

Two widely used turbulence models for jet flow, namely the realizable k- $\varepsilon$  model and the Shear Stress Transport (SST) k- $\omega$  model have been tested.



Figure 1. Centerline and radial profiles of (a) axial velocity and (b) mixture fraction (1: centerline, 2: x/D=4; 3: x/D=30)

The axial velocity and mixture fraction profiles along the centerline and radial at x/D=4 and x/D=30 are shown in Figure 1. Both turbulence models give good results and are suitable for the jet flame simulation. However, it seems that the two models predict slightly faster mixing because the centerline axial velocity profiles drop quicker than experimental data when x/D is larger than 10. This leads to a wider velocity and mixture fraction distribution at x/D=30. In this paper the k- $\omega$  SST model was adopted because it gives slightly better prediction in the core of the downstream. mixing zone, as shown in (a-3) and (b-3) of Figure 1.

#### **Reduced Combustion Mechanism**

Various combustion mechanisms for methane and hydrogen with air have been developed by different research groups (Hughes et al., 2001; Smith et al.; Wang et al., 2007; Ó Conaire et al., 2004). Despite of the high accuracy of these mechanisms in predicting the concentration of both major species and radicals, integrating them for practical usage in most cases such as turbulent combustion modeling is impossible or too expensive due to the large number of species and reactions associated with these detailed mechanisms.

Reduced chemistry covers a wide range turbulence-chemistry interactions with much less species and reactions compared to the original mechanism is thus a logical solution. Sung et al. developed a computer algorithm to generate reduced chemistry automatically and obtained a mechanism including 12 lumped reaction steps and 16 species from GRI-Mech 1.2 (Sung et al., 1998; Frenklach et al.). However, it did not take NO<sub>x</sub> formation into account. Recently a 17-step reduced methane combustion mechanism which accounts for NOx emission (Lu et al., 2008) was developed from GRI-Mech 3.0. This 17step methane combustion mechanism was validated against both premixed and non-premixed flames with extensive parametric variations and was therefore employed in this work.

Development the above-mentioned of mechanisms were based on quasi steady state approximation (QSSA). Hence the reaction rate of each reduced step needs to be calculated from the associated elementary reaction rates in the original mechanism. In the present work, the forward reaction rate constant for each reversible reaction of GRI Mech 3.0 was determined from the pre-exponential factor and activation energy. The backward reaction rate constant was obtained by the software CHEMRev (Rolland and Simmie, 2005) based on the corresponding forward reaction rate constant and the thermodynamic data of the reactants and products. The concentrations of all QSS species were then solved by setting their production and destruction rates to be equal. Finally, the reaction rate of each reduced step was computed and used as source term for the production of non-QSS species in the CFD simulation.

#### Flue Gas Non-gray Radiative Properties

Solving the RTE for an absorbing-emitting gas mixture contained by opaque walls requires the knowledge of the gas radiative properties in terms of the absorption coefficient  $\kappa$ , which varies strongly and rapidly across the spectrum. Using the gray gas radiative model, which uses an averaged absorption coefficient over the entire spectrum, leads in most cases to unacceptable errors (Zhang et al., 2015). For

example in a combustion system the flue gas temperature may be underpredicted up to 100 K or even more due to the gray gas radiative model, which is stated "gray gas myth" (Modest, 2013) and may have some impacts on the NO chemistry.

The most successful wide band model, namely the Exponential Wide Band Model (EWBM) was adopted (Edwards and Balakrishnan, 1973) to calculate flue gas non-gray radiative properties simply because it gives fairly good results but is computationally much less expensive than narrow band models (Grosshandler, 1993; Soufiani and Taine, 1997). In this work the 6 most important absorption bands out of 11 H<sub>2</sub>O and CO<sub>2</sub> absorption bands in EWBM were taken into account in the test furnace simulations. This is because the contribution of other bands are negligible at temperatures lower than 2000 K. Table 1 shows the bands which were considered. Note that the rotational band of H<sub>2</sub>O at 71 µm is only important at lower temperature. It accounts for less than 10% total emissivity of H<sub>2</sub>O when temperature is above 1200 K, which is the typical temperature range for most of the combustion system. Thus usually it can be safely neglected in modeling radiative properties of flue gas. However, the John Zink Hamworthy Combustion test furnace studied in the present work is fed with fuel consisting of 38% hydrogen by weight, resulting in a higher H<sub>2</sub>O concentration than in the combustion exhaust of pure methane. Hence, in this extraordinary case the emitting-absorbing of radiation by H<sub>2</sub>O may be more pronounced and the effect of 71 µm band should be included as well.

Table 1. absorption bands of EWBM considered in thefurnace simulation

Name of the band	Furnace simulation
$H_2O - 71 \ \mu m$	Considered
$H_2O - 6.3 \ \mu m$	Considered
$H_2O - 2.7 \ \mu m$	Considered
$H_2O - 1.87 \ \mu m$	-
H <sub>2</sub> O – 1.38 μm	-
CO <sub>2</sub> – 15 µm	Considered
CO <sub>2</sub> – 10.4 µm	-
CO <sub>2</sub> – 9.4 µm	-
$CO_2 - 4.3 \ \mu m$	Considered
$CO_2 - 2.7 \mu m$	Considered
$CO_2 - 2.0 \ \mu m$	-

Prior to implementing the 6 included bands into CFD simulation of John Zink Hamworthy Combustion test furnace, validation is needed. For this purpose, the total emissivities of  $H_2O$  and  $CO_2$ computed by the 6 included bands were compared with those calculated from full EWBM and a correlation developed by Leckner based on spectrally integrated emissivities (Leckner, 1972). A typical flue gas composition of this furnace was used in all three foregoing calculations, that is, mole fraction of  $H_2O$ and  $CO_2$  equal to 0.25 and 0.04 respectively. The path length of 0.0244 m for the calculation was determined by the averaged beam length over all the cells that are used to discretized the furnace domain.



Figure 2.  $H_2O$  and CO2 emissivities as a function of temperature at path length L=0.0244 m (mole fraction  $x_{H2O}=0.25; x_{CO2}=0.04;$ )

Results depicted in Figure 2 show that the selected 6 bands model yields identical total emissivities for both  $H_2O$  and  $CO_2$  as the full EWBM calculation in a wide temperature range covering most of the flames present in industrial steam cracking furnaces (1000-2000K). It also can be observed that the Leckner's correlation agrees well with the other two models, indicating that the 6 included bands are suitable for the flue gas radiative properties calculation for the test furnaces.

#### John Zink Hamworthy Combustion Test Furnace



#### Figure 3. configuration of the John Zink Hamworthy Combustion test furnace

As shown in Figure 3, the test furnace consists of a radiant section connected to a crossover section and a stack. The fuel gas is a mixture of 62% methane and 38% hydrogen by mass and is fed separately from the combustion air by two floor burners, creating a diffusion flame in the furnace radiation section. The released heat is transferred to 8 vertical cooling water coils positioned on the other side of the furnace facing the floor burners. Three thermocouples are placed in the bottom, middle and the top of the furnace to measure the flue gas temperatures at different positions. In-flame CO probing as well as emission of NOx and CO at the stack are also available. The furnace has two sets of vertically spaced ports on its sidewall close to the cooling water coils which can be used to measure the incident radiation heat flux from the flame at different elevations. It should be noted here that there are 4 rows consisting 3 coils each placed in the crossover section to recover the heat that is not absorbed in the radiation section. However, these coils are not included in the simulation, thus the measured stack temperature cannot be compared with the simulated one.

The furnace was discretized by 7 million cells, on which the mass, momentum and energy conservation equations for a steady-state, compressible, reactive fluid were solved. Gravity was also taken into account since it is reported that it has some influences on the flow pattern of the flue gas (Hassan et al., 2013). The validated models described in the previous sections were integrated to account for the interactions between turbulence, combustion and radiation. Detailed results of the furnace simulation will be discussed in the presentation.

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# Non-linear regression of the thermochemical state-space onto a reduced number of principal components

Benjamin J. Isaac<sup>a</sup>, Mohammad Rafi Malik<sup>b</sup>, Alessandro Parente<sup>b\*</sup>

<sup>a</sup> – Department of Chemical Engineering, University of Utah, Salt Lake City, UT, 84112, USA

<sup>b</sup> - Service d'Aéro-Thermo-Mécanique, Université Libre de Bruxelles, Bruxelles, Belgium

- Alessandro.Parente@ulb.ac.be

#### Abstract

Modeling the physics of combustion remains a challenge due to a large range of temporal and physical scales which are important in these systems. Detailed chemical kinetic mechanisms are used to describe the chemistry involved in the combustion process yielding highly coupled partial differential equations for each of the chemical species used in the mechanism. Recently, Principal Components Analysis (PCA) has shown promise in its ability to identify a low-dimensional manifold describing the reacting system. Several PCA-based models have been developed which may be well suited for combustion problems; however, several challenging aspects of the model must be addressed.

The present work seeks to advance the understanding and application of the PC-transport approach by analyzing the ability to parameterize the thermo-chemical state with the PC basis using various non-linear regression methods. In order to demonstrate the accuracy of the method within a numerical solver, auto-ignition and unsteady perfectly stirred reactor (PSR) calculations are shown using the PC-transport approach. The auto-ignition and PSR analysis extend previous investigations by the Authors to more complex fuels (e.g. methane, propane), showing the ability of the approach to deal with relatively large kinetic mechanisms. Lastly, the potential of exploiting the developed approach in a CFD solver is demonstrated by means of the simulation of a two-dimensional syngas jet.

#### Keywords

Combustion; Nonlinear Regression; Low-dimensional manifolds; Principal Component Analysis.

#### Introduction

The numerical modeling of turbulent combustion is a very challenging task as it combines the complex phenomena of turbulence and chemical reactions. This study becomes even more challenging when large detailed kinetic mechanisms are used in order to understand some special features such as pollutant formation. A simple fuel such as CH4 has been accurately described using 53 species and 325 chemical reactions (Smith et al.). More complex fuels require increasingly complex chemical mechanisms. Each resolved chemical species requires a conservation equation which is a coupled, highly nonlinear partial differential equation. Such systems are only possible to solve under very limited situations at this time due to computational costs. Therefore, there is a need for methods allowing to efficiently parameterizing the thermo-chemical state of a reacting system with a reduced number of optimal reaction variables. Among those, Principal Component Analysis (PCA) appears as an ideal candidate to fulfill the purpose. As a matter of fact, PCA offers the possibility of automatically reducing the dimensionality of data sets consisting of a large number of correlated variables, while retaining most of the variation present in the original data. Several advantages of PCA include: its ability to identify orthogonal variables which are the best linear

representation of the system; its ability to reduce in dimensionality requiring fewer coordinates; and the ability to do the analysis on canonical systems, such as the counter diffusion fame or empirical data-sets containing highly complex turbulent chemistry interaction. A methodology based on PCA was proposed (Parente et al., 2009) for the identification of the controlling dynamics in reacting systems and for the consistent reduction of very large kinetic mechanisms. In addition, several combustion models have been proposed based on the concepts from PCA. Sutherland and Parente (Sutherland and Parente, 2009) derived transport equations for the principal components (PCs), and discussed the feasibility of a model where the PCs are used directly to construct state-space variables. The PCA-based modeling approach was enhanced (Mirgolbabaei and Echekki, 2013; Einbeck et al.; Yang et al., 2013) by combining PCA with nonlinear regression techniques, allowing a nonlinear mapping of the thermo-chemical state and the corresponding source terms onto the basis identified by the principal components, to account for the non-linear nature of chemical manifolds and, thus, maximize the potential size reduction provided by the method. In a previous study (Isaac et al., 2014), the authors showed the potential of PC-transport based combustion models coupled with non-linear regression techniques. The model was tested on an unsteady calculation of a perfectly stirred reactor (PSR) burning syngas. In particular, it has been showed that Gaussian Process Regression (GPR) technique produced the most accurate reconstruction, showing remarkable accuracy for the prediction of temperature and major and minor species with 2 transported variables instead of 11. The approach was also tested for the first time within a CFD solver. The present work seeks to advance the understanding and application of the PCtransport approach by applying this method to a more complex fuel such as methane. This analysis is carried out on the solution of an unsteady PSR calculation using the PC-transport approach with non-linear regression (GPR). Also, an a priori analysis is done on the different scaling methods used in PCA and on the relative importance of the species source terms.

#### Theory

In order to perform principal component analysis, a data-set consisting of n observations and Q independent variables is organized as an  $n \times Q$  matrix **X**. The data **X** is centered to zero by its corresponding means and scaled by the diagonal matrix, **D**, containing the scaling value for each of the k variables:

$$\mathbf{X}_{\mathrm{SC}} = (\mathbf{X} - \overline{\mathbf{X}})\mathbf{D}^{-1} \tag{1}$$

The principal components  $(\mathbf{Z})$  are then identified by performing an eigenvalue decomposition of the covariance matrix of:

$$\frac{1}{Q-1}\mathbf{X}^{sT}\mathbf{X}_{s} = \mathbf{A}^{-1}\mathbf{L}\mathbf{A}$$
(2)

The original state-space is then projected on the eigenvector matrix **A**:

$$\mathbf{Z} = \mathbf{X}^{\mathbf{s}} \mathbf{A} \tag{3}$$

The original state-space can then be uniquely recovered using the previous equation:

$$\mathbf{X}^{\mathbf{s}} = \mathbf{Z}\mathbf{A}^{\mathrm{T}} \tag{4}$$

Then, using a subset of the basis matrix  $\mathbf{A}$ , denoted as  $\mathbf{A}_{\mathbf{q}}$  and applying the previous equation, an approximation of the original centered and scaled statespace can be made using the following:

$$\mathbf{X}_{\mathbf{s}} \approx \mathbf{Z}_{\mathbf{q}} \mathbf{A}_{\mathbf{q}}^{\mathrm{T}}$$
 (5)

In the PC analysis, the largest eigenvalues correspond to the first columns of A. This means the largest amount of variance in the original variables is described by the first PCs. Accordingly, when one truncates the basis matrix  $(A_q)$ , the resultant approximation from Eq. (5) may yield very accurate results, while representing the system with fewer variables. Transport equations for the PCs can be formulated from the state-space variable equations (Isaac et al. (2014):

$$\frac{\partial}{\partial t} \left( \rho Z_q \right) + \frac{\partial}{\partial x_i} \left( \rho u_i Z_q \right) = \frac{\partial}{\partial x_i} \left( D_{Z_q} \frac{\partial}{\partial x_i} (Z_q) \right) + s_{Z_q} \quad (6)$$
$$s_{Z_q} = \frac{1}{\rho} \sum_{k=1}^Q \frac{R_k}{d_k} A_{kq} \qquad (7)$$

where  $R_k$  is the source term of the  $k_{th}$  species transport equation.

In PCA-based combustions models, one of the major weakness is that a linear model is trying to describe a highly non-linear process. In order to take full advantage of the PC analysis, a nonlinear mapping to the linear underlying surface by using nonlinear regression was proposed (Biglari and Sutherland, 2012). This allows to fully utilize the underlying manifold identified by the principal component analysis.

#### **Regression Models**

In this study, the state-space variables and the PC source terms are mapped to the PC basis using nonlinear regression:

$$\phi \approx f_{\phi}(Z_q) \tag{8}$$

Where  $f_{\phi}$  is the nonlinear regression function and  $\phi$  represent the state-space variables. The following regression techniques are investigated:

- *Linear Regression Model (LIN)* in which the state-space is mapped to the PC using a linear function (Cleveland et al., 1992).
- *Mutivariate Adaptive Regression Splines* (*MARS*) where the model is build from product spline basis functions (Friedman, 1991).
- Artificial Neural Networks (ANN) that uses the concept of networking various layers of estimation resulting in a highly accurate output layer (Pao, 2008).
- Support Vector Regression (SVR) which is a subset of support vector machines (SVM). The idea behind SVR is again to create a model which predicts  $s_Z$  given Z using learning machines which implement the structural risk minimization inductive principle (Smola and Scholkopf, 2004).
- *Gaussian Process Regression (GPR)* is based on the idea that dependent variables can be described by a gaussian distribution (Nguyen-

#### **Test Cases**

The proposed approach was demonstrated on the unsteady solution of a perfectly stirred reactor (PSR) and a 2D jet flame.

For the PSR, the solution from the full set of equations was compared to the standard PC-transport approach, and the PC-transport approach using nonlinear regression. Two different fuels were investigated: a syngas-air and a methane-oxygen mixture. The data set for the PCA were generated by setting the inlet condition at 300K with a stoichiometric mixture of fuel and air for the syngas and of fuel and oxygen for methane. The vessel was initialized at equilibrium conditions (constant pressure and enthalpy), and multiple simulations were performed by varying the residence time in the vessel. All of the unsteady data for the various simulations is used collectively for the PCA analysis. The mechanisms used were a 11 species and 21 reactions for the syngas (Davis et al., 2005), and the GRI 3.0 (Smith et al.) for the methane, without the NOx species. The inlet conditions for the reactor are set at an equivalence ratio of 1 with a temperature of 300K. The initial conditions for the reactor are set at the equilibrium conditions of the inlet and the system is run until a steady-state solution is reached. The PSR is modeled assuming constant volume, residence time and pressure. The PCA process described in the Theory section is then applied to the data to create the basis matrix  $A_q$ , and the regression functions  $f_{\phi}$  for the statespace variables,  $\phi$ . The approach is then tested with various values of  $\tau$ , which were not used when creating the data-set. The implementation of the PSR equations was done using MATLAB together with the Cvode toolbox. The temporal solution to the equations is obtained using the Newton nonlinear solver, and the BDF multistep method.

For the 2D syngas jet flame, the jet's inlet boundary consists of a partially premixed mixture of syngas and air with a mixture fraction of 0.79, at equilibrium conditions (T  $\approx$  1025 K). The jet has a velocity of 25 m/s with a co-flow of air at 0.1 m/s and 300 K. The domain is a 2D square of 0.5 m<sup>2</sup> represented with 1500<sup>2</sup> grid points, and a jet diameter of 0.01 m. The simulation is performed within the Uintah Framework using the simulation software ARCHES. The explicit algorithm of ARCHES is limited to a maximum time-step size of 1e – 7 s, reaching a physical time of 0.25 s.

#### **Results and Discussion**

#### Syngas case

Table 1 shows the regression results for  $s_{Z_1}$  as a function of Z, with q = 2 and q = 3 for the syngas

case.

Table 1: Nrms error and  $R^2$  statistics for the prediction of the first source term while using pareto

Method	Nrms (q=2)	<i>R</i> <sup>2</sup> (q=2)	Nrms (q=3)	<i>R</i> <sup>2</sup> (q=3)
LIN	0.99	0.02	0.67	0.55
MARS	0.30	0.91	0.26	0.93
ANN	0.22	0.95	0.20	0.96
SVR	0.23	0.95	0.19	0.97
GPR	0.22	0.95	0.18	0.97

As expected, the linear regression method has difficulty mapping the highly nonlinear dependent variables. Complex methods also struggle with the mapping while q = 2. When moving to q = 3, the later 3 methods are beginning to show higher accuracy. In this particular case, GPR produces the most accurate reconstruction. Figure 1 shows the temperature profile for the system.



Figure 1: Temperature profile for the syngas case

The markers show the steady-state solution for a given  $\tau$  using the PC-transport model. The underlying solidlines in the figures show the full solution calculated over a range of residence times. The regression of  $\phi$  is carried out using q = 2 resulting in  $R^2$  of 0.9995 or higher for all variables including  $s_{Zq}$ . The simulations are then performed with 2 transport equations instead of 11, yielding a significant reduction. The results show remarkable accuracy for the model with regression over the range of residences times for the predicted temperature. The 2D syngas jet flame is carried out solving for 2 transport equations, given an accurate reconstruction of  $\phi$ . Figure 2 shows the temperature field at *t*=0.25 s.


Figure 2: Temperature field from the ARCHES calculation at t=0.25s

#### Methane case

First, the effects of various scaling methods were tested. The methods analyzed were: standard scaling, range, pareto, vast and level. The  $R^2$  coefficient was used to assess the accuracy of the scaling method. Level scaling gave the best results for the minimum  $R^2$  while varying the number of PCs retained. Figure 3 shows the temperature profile for the methane case, using the full set of PC (34 components) and a reduced set of 19 components. Similarly to the syngas case, a large number of components in needed when transporting the PCs, if the source term is directly computed. Currently, the non-linear regression approach is being extended to the methane case, with the final objective of simulating a 2D turbulent methane jet.



#### Conclusion

It is evident that the linear PC model in conjunction with a nonlinear regression has the potential of delivering very accurate state-space variables as well as reaction rates for a given system of interest. The various nonlinear regression methods analyzed in this work have shown the ability to produce accurate estimation even when using a lower number of Z. In particular, the SVM and GPR methods have shown improved accuracy for estimating  $\phi$ . This work also includes the first demonstrations of the PC-transport model using nonlinear regression within a numerical solver. The approach was demonstrated for the first time within a CFD solver using syngas. The CFD calculation can be considered a good proof of concept for the proposed approach. The extension of the approach on a more complex fuel (methane) using a simple reactor (PSR) also showed promising results, which will be further investigated and extended to a full CFD calculation.

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### MATHEMATICS OF (THE THERMODYNAMICS OF) MIXED GASES ADSORBED IN A ZEOLITE

Fei Wang, Yasukazu Kobayashi, Yuxin Li, Dezheng Wang<sup>\*</sup>, and Yao Wang Department of Chemical Engineering, Tsinghua University Beijing, 100084 China Email: wangdezheng@tsinghua.edu.cn

*Abstract* Adsorption of methanol, dimethyl ether, ethene and propane individually in SAPO-34 with the adsorption isotherm measured simultaneously with the calorimetric (adsorption heat versus coverage) curve showed there were two phases of adsorption: Type 1 adsorption on the acid sites at lower pressures and Type 2 adsorption elsewhere by physisorption at higher pressures. Although binary gas mixture experiments showed that only the ideal adsorbed solution theory (IAST) gave correct surface concentrations, that due to the two phases of adsorption, the multicomponent Langmuir isotherm (MLI) for competitive adsorption was incorrect at high concentrations, but the MLI should be used for concentration calculations for kinetics while the IAST should be used for concentration calculations for diffusivities.

Keywords IAST, Competitive Adsorption, Multicomponent Langmuir Isotherm.

#### Introduction

A solid catalyst deals with gas mixtures, so getting the adsorbate concentrations in a mixture is important. Although this is gas-surface thermodynamics, the result is used in kinetics when a slow step uses an adsorbed species. For example, the methanol-to-olefins (MTO) process has methanol protonation as a slow step in the reaction network, and its kinetic expression is first order in methanol concentration. At high conversion when the reaction occurs in a mixture of methanol and olefins, it is the surface concentration of methanol in the mixture that is needed. The correct use of the thermodynamics of individual adsorbates to get the correct concentrations in the mixture will give correct activity and selectivity.

It is known that the multicomponent Langmuir isotherm (MLI) for competitive adsorption can be incorrect for calculating the surface concentrations in a mixture (Myers and Prausnitz, 1965). In describing the adsorption equilibrium in separation equipment, the MLI is seldom used, presumably because it would be incorrect, which is broad albeit indirect admission of the inadequacy of the MLI. Bartholdy et al. (2013) did not commend the MLI after a comparison of the predictions of the MLI, IAST and other mixed gases models. Krishna and Baur (2005) and Hansen et al. (2009) computed that incorrect equilibrium concentrations due to the MLI would give wrong kinetics concentrations.

On the other hand, for gas-solid catalyzed reactions, the textbooks teach us to use the MLI to calculate the surface concentration of a component in a mixture despite its being known that MLI calculations are not consistent with solution thermodynamics, i.e., they can differ from those using equations that include solution thermodynamics, e.g., ideal adsorbed solution theory (IAST). IAST includes heterogeneous solution thermodynamics by imposing Raoult's Law on the gas

• To whom correspondence should be addressed

and adsorbed phase compositions. Thus the reason why the MLI is still widely used, and whether it is correct for heterogeneous catalytic kinetics should be addressed. Its usage is probably because the MLI is consistent with thermodynamics when the monolayer capacity is the same for all species. For competitive chemisorption on many catalysts, the monolayer capacity or site density is the same for all species and the MLI can be used. Here we shall examine the sense in which this true in a zeolite and argue for its use although in the zeolite physically adsorbed molecules are abundant, and the MLI concentrations are incorrect when these are included.

#### Experimental

The catalyst used was a SAPO-34 zeolite described in Li et al. (2014). Its surface area, pore volume and pore size were, respectively, 1247 m<sup>2</sup>/g, 0.297 cc/g and 0.552 nm. The particle sizes were 1 to 2  $\mu$ m. The acid site density was calculated from SEM-EDS and NH<sub>3</sub>-TPD data to be 1.0 mml/g.

The measurement of adsorption isotherms and calorimetric (adsorption heat versus coverage) curves were performed on a combination adsorption volumetric manometry and Tian-Calvet microcalorimeter apparatus described in Kobayashi et al. (2014b). The adsorbates were methanol, dimethyl ether (DME), ethene, propane, and a binary methanol-DME mixture with the methanol:DME proportion of 63:37 mol% and a binary DME-ethene mixture with the DME:ethene proportion of 57:43 mol%. Our interest in this system is for the MTO process. Adsorption was carried out after the sample was preheated at 400 °C for 5 hours under vacuum, then first saturated by the gas to cover the sites of irreversible adsorption and evacuated so that the subsequent measurement measured only the reversibly adsorbed gas. During the adsorption experiments with a gas mixture, a mass spectrometer (MS) was used to analyze the residual gas phase composition, which was used to calculate the experimental adsorbed phase

concentrations. The dead volume of the sample call was 40 ml, which was large enough to allow the gas phase to be sampled by the MS with negligible loss of gas. Equilibrium in the gas phase was verified before the next dose by comparing MS samples for successive times until there was no change in the gas phase. Equilibrium was usually established within two to three hour when an alkane was used, and much quicker otherwise.

#### **Results and Discussion**

We show using the SAPO-34 zeolite sample that the adsorption in it first occurs on the acid sites. However, unlike many types of solid or supported catalysts where adsorption reached saturation when the active sites were all occupied, in the SAPO-34 zeolite, after the acid sites were occupied, more molecules were still adsorbed as weakly adsorbed species. This is shown by the methanol adsorption data in figures 1 and 2, previously reported in Kobayashi et al (2013), for which we can now give a more complete discussion consistent with further data.



Figure 1. Adsorption isotherms of methanol on SAPO-34 zeolite at 25 °C ( $\circ$ ), 60 °C ( $\blacktriangle$ ) and 100 °C ( $\Box$ ).



Figure 2. Calorimetric curves of methanol adsorbed on SAPO-34 at 25 °C ( $\circ$ ), 60 °C ( $\blacktriangle$ ) and 100 °C ( $\Box$ ).

The dotted lines show the acid site density of 1.0 mmol/g of the SAPO-34. The vertical arrows in figure 2 are given to guide the eye to see the surface concentration after which there was a sharp drop in the

adsorption heat. The vertical arrows in figure 1 indicate where these surface concentrations occur on the adsorption isotherm. The salient feature of figure 1 is that the adsorption isotherm did not reach saturation at these surface concentrations. Since the analysis of calorimetric curves (Auroux, 1994) for a zeolite would take an adsorption heat decrease following a plateau to indicate the saturation of the acid sites, our interpretation of the combined data of figures 1 and 2 is that there is a latter adsorption of weakly adsorbed species, that this is a significant fraction of the total adsorption, and this adsorption occurred after most acid sites were occupied and so it is apart from the first adsorption. To account for this, the zeolite is treated as a dual site adsorption system comprising Type 1 and Type 2 adsorption phases. Type 2 adsorption happens later and it is not adsorption on an acid (Type 1) site although it is also in the confined space in the zeolite, possibly as floating molecules also present inside the cages.

A feature in figure 1 that can be misleading if these isotherms were used to help understand reaction kinetics is that the saturation concentrations on the acid sites, indicated by the arrows, were higher than the acid site density of 1.0 mmol/g. This was due to two complications: there was some irreversible adsorption and the adsorbate can form a cluster of molecules on a site. After subtracting irreversibly adsorbed amounts, the stoichiometry of reversibly adsorbed methanol to acid site was 3.3, 2.2 and 1.3 at 25, 60 and 100°C, respectively, that is, the adsorption stoichiometry > 1.0. This has been discussed in Kobayashi et al. (2013, 2014a) and references therein as being due to the adsorption of methanol as molecular clusters stabilized by hydrogen bonding. A calorimetric feature that supported this was that there was an increase in adsorption heat before the decrease at saturation. Both these complications will not be further discussed because they were deemed to be features of only low temperature adsorption, and at 100°C, the adsorption stoichiometry approached 1.0, they would not affect the reaction kinetics that occur at higher temperatures.

The adsorption of the other gases that were studied all showed a similar qualitative behavior, namely, the adsorption isotherm did not reach saturation at the surface concentration where the calorimetric curve indicated saturation of the acid sites. These also showed



*Figure 3. Adsorption isotherm of ethene on SAPO-34 at 25 °C (○); 45 °C (Δ); and 65 °C (■).* 



*Figure 4. Calorimetric curve of ethene adsorbed on SAPO-34 at 25 °C* ( $\circ$ ); *45 °C* ( $\Delta$ ); *and 65 °C* ( $\blacksquare$ ).

that the adsorption in the zeolite comprised Type 1 and Type 2 adsorption phases. Another example of this using ethene adsorption data from Wang et al. (2015) is shown by the combined data in figures 3 and 4. Ethene differs from methanol in being nonpolar and so it adsorbs on the acid site by induced dipole interactions, which is a much weaker adsorption with a smaller adsorption heat. It is probably due to this that the calorimetric curves in figure 4 did not show a sharp drop like those in figure 2, but they showed a gradual drop-off. However, on comparing the arrows in figure 4, used to guide the eye to see the surface concentrations after which the dropoff began, with the corresponding arrows in figure 3 that indicate these surface concentrations on the adsorption isotherms, it is also evident that the adsorption isotherms in figure 3 did not reach saturation at these surface concentrations. Thus, ethene adsorption in the zeolite also comprise Type 1 and Type 2 adsorption phases.



Figure 5. Fitting ethene adsorption at  $25^{\circ}C(\blacksquare)$ ;  $45^{\circ}C(\bullet)$ ; and  $65^{\circ}C(\blacktriangle)$  with Langmuir (dashed lines) and dual (Type 1 and Type 2) site isotherms (solid lines).

Figure 5 shows the best fit curves to the ethene adsorption data using the Langmuir isotherm (dashed lines) and comparing it with the dual site isotherm comprising Type 1 and Type 2 adsorption phases. The limited adsorption pressure range made it not so obvious for the data at  $45^{\circ}$ C and  $65^{\circ}$ C in figure 5 but actually,

the dual site isotherm gave the better fits. This is because the dual site isotherm curve can go up, as the adsorbed amount does, at higher pressure, while the (single site) Langmuir isotherm must flatten to a plateau. This points out a problem that can occur with adsorption data collected over a limited pressure range, namely, they can be mistakenly fitted with the single site Langmuir isotherm. With the correct dual site isotherm, figure 6 shows by direct computation using the MLI and IAST that due to the separate adsorption in dual adsorption processes, the MLI and IAST surface concentrations are different although the acid site density for Type 1 adsorption is the same for all the adsorbates (Wang et al., 2015). The pure gas isotherm parameters used for



Figure 6. Surface concentrations in a mixture calculated by MLI and IAST when adsorption occurs on dual sites.

the data in figure 6 were: for adsorbate A,  $C^{sat} = 1.0$  mmol/g,  $b_1 = 0.50$  kPa<sup>-1</sup>,  $K_1 = 0.001$  mmol/g/kPa; for adsorbate B,  $C^{sat} = 1.0$  mmol/g,  $b_2 = 0.038$  kPa<sup>-1</sup>,  $K_2 = 0.010$  mmol/g/kPa. These parameters roughly describe the case where adsorbate A is a small, polar molecule and adsorbate B is a longer, non-polar molecule, e.g., methanol and ethene, respectively.

In order to interpret this result for its use in reaction kinetics, it is necessary to examine the IAST equations to see why the calculated concentrations were different. With no loss of generality, the IAST for a binary mixture can be used. The IAST sets the spreading pressure ( $\pi$ ) to be the same for all the components,

$$\frac{\pi A}{RT} = \int_0^{P_1^0} \frac{C_1}{P} dP = \int_0^{P_2^0} \frac{C_2}{P} dP$$
(1)

The first equality says that  $\pi$  is calculated from the Gibbs isotherm, and the second equality says ( $\pi$  due to component 2) = ( $\pi$  due to component 1). In Eq. (1),  $P_i^0$  is the gas pressure that gives the spreading pressure  $\pi$ . If the Langmuir isotherm is used for  $C_1$  and  $C_2$  in Eq. (1),

$$\frac{\pi A}{RT} = C^{sat} \ln \left(1 + b_1 P_1^0\right) = C^{sat} \ln \left(1 + b_2 P_2^0\right)$$
(2)

 $P_i^0$  is not known, and it has to be solved for. Equation (2) shows that doing this requires using the Langmuir isotherm adsorption constants ( $b_i$ ) to satisfy Eq. (3):

$$b_1 P_1^0 = b_2 P_2^0 \tag{3}$$

Yang showed that when Eq. (3) is used in the IAST's form of Raoult's law, the MLI results. Thus, when the individual adsorbates obey the (single site) Langmuir isotherm, the MLI and IAST compute the same surface concentrations. The converse can also be shown when the individual adsorbates do not obey the single site Langmuir isotherm, but a dual site isotherm, e.g.,

$$C_{1} = C^{sat} \frac{b_{1}P}{1+b_{1}P} + K_{1}P$$
(4)

In Eq. (4), the second site used Henry's law because the adsorption on it is not strong and the pressure is not very high. The use of Eq. (4) in Eq. (1) will give

$$C^{sat} \ln (1 + b_1 P_1^0) + K_1 P_1^0 = C^{sat} \ln (1 + b_2 P_2^0) + K_2 P_2^0 \quad (5)$$

which will not result in Eq. (3), and there is then no equivalence of MLI and IAST.

From the above results, the conclusions are that the dual site isotherm should be used for gas adsorption in SAPO-34 zeolite, and this will result in the MLI and IAST giving different surface concentrations. The results in Kobayashi et al. (2014a) and Wang et al. (2015) and in the literature in the references therein showed that when the MLI and IAST differ, it is the IAST that gave the correct surface concentrations.

It would seem, therefore, that the IAST should be used for getting the surface concentrations for reaction kinetics calculations. Here, we argue that it is actually the MLI that should be used. The key point to consider is the nature of the second site in the dual site isotherm. Wang et al. (2015) viewed this as due to that there is no free gas movement in the zeolite such as exists over an open surface. The confinement of molecules inside the zeolite results in additional physisorbed species that do not exist on an open surface where the space above the open surface allows physisorbed species to desorb, and thus its (the open surface's) weakly physisorbed concentration will be low and negligible. In contrast, in a zeolite, the adsorption of more molecules than there are acid sites in a zeolite is well known. The excess molecules, in excess of the acid sites, would be due to entrapment in the zeolite where the molecules remain as physisorbed molecules. However, if this is true, it could also be said that these excess molecules would be merely spectators that do not take part in the catalyzed reactions. Thus, they should not be included in the concentration of reacting molecules. So, with respect to reaction kinetics, it should be the MLI that is to be used for getting the reacting surface concentrations, but with the proviso that it used the first Langmuir isotherm in a dual site model. However, the kinetics in zeolites are often affected by diffusion limitation. We can argue that when the diffusivity is concentration dependent, for this

concentration, the MLI cannot be used and the IAST should be used.

#### Conclusion

Adsorption of gases in SAPO-34 occurs on Type 1 sites (acid sites) and on Type 2 sites. Although the IAST gives the correct total concentration of individual adsorbates, this total includes physisorbed molecules on Type 2 sites, and the multicomponent Langmuir isotherm for Type 1 sites is to be used for reacting surface concentrations because catalysis uses acid sites.

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## New active sites or old surface species? A methodology to understand the kinetics behind dynamic behavior of gas-solid catalytic reactions using feed switching experiments

S.K Wilkinson<sup>1,2,\*</sup>, L.G.A. van de Water<sup>1</sup>, M.J. Simmons<sup>2</sup>, E.H. Stitt<sup>1</sup>, M.J. Watson<sup>1</sup>

1. Johnson Matthey Technology Centre, Belasis Avenue, Billingham, UK, TS23 1LH 2. School of Chemical Engineering, University of Birmingham, Birmingham, UK, B15 2TT

#### Abstract

For a given heterogeneous catalytic process, it can be very easy to trivialise the descriptions of underpinning reaction mechanism(s). Examples include simplifications of micro-kinetic models, particularly in delivering a steady state description, or in the lumping of multiple reaction mechanisms. As a result, gaining an adequate understanding of the link between catalyst structure, feed composition and its impact on the generation of catalytically active sites can become limited without a more detailed investigation.

A case study of methanol synthesis over Cu-based catalysts is presented. A chief aim is to address the effect of  $P_{CO}/P_{CO2}$  ratio in the feed on catalyst functionality. A steady state kinetic model description is developed for feeds with  $P_{CO}/P_{CO2}$  ratios as high as 10 based using the micro-kinetic based model of Vanden Bussche and Froment, (1996) over metallic Cu. Under these conditions, the source of carbon in methanol can be either CO or CO<sub>2</sub> but ultimately the kinetic model suggests that the same mechanistic pathway is followed. Meanwhile, behaviour under CO/H<sub>2</sub> conditions (i.e. <u>no</u> CO<sub>2</sub> in feed) was found to be significantly different. Only Cu-based catalysts with a reducible support (e.g. ZnO) showed methanol synthesis activity in these conditions, suggesting Cu surface area alone is not the only metric in generating activity in this scenario. The need for micro-kinetic, step-by-step models is discussed as necessary under CO/H<sub>2</sub> conditions due to the inherent changes to catalyst state that these reaction conditions can have.

Keywords: micro kinetics, transient, active site, surface species, methanol synthesis

#### Introduction

For a given heterogeneous catalytic process, it can be very easy to trivialise the descriptions of underpinning reaction mechanism(s). Examples include simplifications of micro-kinetic models, particularly in delivering a steady state description, or in the lumping of multiple reaction mechanisms. In recent years, increased use of transient kinetic analysis techniques has improved this position, allowing the fundamentals of catalytic performance to be understood both as a function of catalyst composition but also the feed conditions imposed on it. Both factors are often intrinsically linked and the generation of active sites on catalytic material can be strongly driven by the reaction conditions employed.

The synthesis of methanol (CH<sub>3</sub>OH) from syngas (mixtures of CO/CO<sub>2</sub>/H<sub>2</sub>) exemplifies this as it features a catalyst whose active sites are generated *in situ*. The industrial process uses a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst which operates at elevated pressure (50 – 80 bar) and mild temperatures (< 573 K). Three key reactions can take place which can be equilibrium limited in the conditions of interest:

 $CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$  (1)

$$CO_2 + H_2 \leftrightarrow CO + H_2O \tag{2}$$

$$CO + 2H_2 \leftrightarrow CH_3OH$$
 (3)

Significant research been directed at understanding the reaction mechanism and nature of

the active site for methanol synthesis. Significantly, the works of Liu *et al.*, (1985) and Chinchen *et al.*, (1986) demonstrated the prevalence of producing methanol via  $CO_2$  over Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> and that activity of these catalysts were directly related to the copper surface area of the catalyst. The choice of support (e.g. Al<sub>2</sub>O<sub>3</sub>, ZnO, SiO<sub>2</sub>) was purely seen as a means to maintain a stable dispersion of metallic copper. A later work by Vanden Bussche and Froment (1996) demonstrated a robust mechanistically driven kinetic model for CO<sub>2</sub> hydrogenation and reverse water gas shift (RWGS) over a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst for a wide range of conditions (Pressure = 15 – 51 bar, Temp. = 453 – 553 K, P<sub>CO</sub>/P<sub>CO2</sub> = 0 – 4).

Such descriptors are effective to a point but do not fully explain observations at high (>10)  $P_{CO}/P_{CO2}$ ratios observed by Klier *et al.*, (1982) and Sahibzada *et al.*, (1995). Here, an increase of intrinsic methanol productivity is seen in *low*-CO<sub>2</sub> content feeds but a sudden drop to a much lower productivity is observed in CO<sub>2</sub>-*absent* feeds. This non-linearity suggests that the catalyst surface or mechanistic pathways to methanol may be altered in this range of conditions.

The work by Bos et al., (1989) attempted to decouple the kinetics for equations (1) and (3) however catalyst stability issues were encountered when using CO/H<sub>2</sub> feeds. A time and reaction conditions dependent elution of CO<sub>2</sub> and H<sub>2</sub>O from the catalyst was observed. Frost (1988) postulated that feeds such as CO/H<sub>2</sub> can reduce interfacial sites between a metal and a reducible support. For Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>, reduction by

CO to form a Cu-[]-Zn interface was postulated to develop  $Cu^{\delta_+}$  sites which can synthesise methanol from CO. These interfacial sites have been shown to have a limited life in the presence of CO<sub>2</sub>. A recent work by Vesborg *et al.*, (2009) showed a transient overproduction of methanol when switching from CO/H<sub>2</sub> to CO/CO<sub>2</sub>/H<sub>2</sub> feeds. Vanden Bussche and Froment (1994) showed this was attributed to a fast CO<sub>2</sub> hydrogenation mechanism over these interfacial site.

#### Aims

In this study, a methodology is presented using discretised micro-reactor testing and kinetic analysis to probe the linkage between catalyst formulation and reaction conditions. In light of the prior art, there is a need to develop a more encompassing framework for methanol synthesis catalysis over Cu-based catalysts at industrially relevant conditions. The aims of this paper are thus:

- Develop tools to probe the link between catalyst formulation (physical descriptors), catalyst functionality and feed conditions.
- Discriminate between mechanisms for methanol synthesis under CO/CO<sub>2</sub>/H<sub>2</sub> and CO/H<sub>2</sub> feeds.
- Understand the feed condition limits of describing methanol synthesis via CO<sub>2</sub> hydrogenation over metallic copper.
- Develop experimental and modeling methods to probe catalyst state and functionality under CO/H<sub>2</sub> feed conditions.

To achieve these aims, Cu-based catalysts are exposed to different 'steps' in conditions to track behaviour, as shown in Figure 1:



Figure 1: Conditions Cu-based catalysts are exposed to in this study

#### **Materials and Methods**

Three catalysts precursors were chosen for this study, which were all ground into powder form (particle size range  $180 < d_p < 355 \mu$ m). The catalysts were CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> (60/30/10 by mass), CuO/ZnO (34/66) and CuO/Al<sub>2</sub>O<sub>3</sub> (25/75). The catalysts had 'as received' BET surface areas of 97.9, 31.8 and 205.1 m<sup>2</sup> g<sup>-1</sup> and Cu surface areas of 32.4, 16.0 and 6.4 m<sup>2</sup> g<sup>-1</sup> respectively. The latter was determined by  $N_2O$  reactive frontal chromatography (Narita *et al.*, 1982).

Reaction studies using the catalyst precursor formulations described above were carried out in fixedbed, down-flow, steel micro-reactors. Six parallel tubes were used with inner diameter of 3 mm and length of ~20 cm. Outlet gases from the reactors were analysed using an IR analyser. Catalyst tests were carried out under the following range of conditions:

Temperature: 453 - 493 K Total Pressure: 15 - 35 bar Flow Rate (STP): 7.5 L h<sup>-1</sup> Gas comp.: 3 % CO / 0 - 3% CO<sub>2</sub> / 67% H<sub>2</sub> / bal. N<sub>2</sub> Reactor Inlet CO/CO<sub>2</sub> ratios:  $1, 3, 10, \infty$ Catalyst mass: 0.125 - 0.500 g

During testing, the catalyst was tested under intrinsic reaction conditions. The absence of mass and heat transport gradients was thoroughly verified using classic literature methods (Perez-Ramirez *et al.*, 2000).

At the start of any test presented, the precursor material was subjected to a temperature programmed reduction in 2%  $H_2$  /  $N_2$ . The materials were taken to a maximum temperature of 498 K during this process. It was verified by back calculation of  $H_2O$  derived during this process that the entirety of the CuO component had been fully reduced to Cu<sup>0</sup>.

In all results presented, the catalysts were tested in a parallel difference setup, as shown in Figure 2. This allows for effective axial discretisation of catalyst performance by mass under both steady and non-steady state conditions (Wilkinson *et al.*, 2013):



Figure 2: Parallel difference setup for testing copperbased catalysts. Cat. denotes catalyst and SiC denotes silicon carbide (inert) packing

Parameter estimation within the kinetic models was carried out using Athena Visual Workbench<sup>®</sup> software. All response variables in the methanol synthesis reaction network are dependent on multiple reactions and so the models must be solved implicitly using a set of differential equations. Kinetic model parameters for isothermal datasets were solved using a non-linear least squares approach, whilst a

Bayesian estimation approach was used for the temperature dependent ones.

To minimise cross-correlation between activation energy  $(E_a)$  and pre-exponential factor  $(A_i)$  parameters, a re-parameterised Arrhenius equation was used:

$$k_{i} = A_{i,ref} \cdot \exp\left(\left(\frac{E_{a}}{T_{ref} \cdot R}\right) \cdot \left(1 - \frac{T_{ref}}{T}\right)\right)$$
(4)

Where  $T_{ref}$  denotes reference temperature and  $A_{i,ref}$  is the value of the rate constant  $k_i$  at  $T_{ref}$ . An analogous approach was used for any Van't Hoff adsorption equilibrium terms. Equilibrium constants, taken from Graaf *et al.*, (1986), were utilised in all kinetic equations to account for thermodynamic limitations. Gaseous components were also checked for non-ideal behaviour. Using the Soave-Redlich-Kwong equation of state, all gases tested were found to have compressibility factors between 0.99 and 1.01, so partial pressures rather than fugacities were used in this study.

#### **Results and Discussion**

#### Kinetics for CO/CO<sub>2</sub>/H<sub>2</sub> feeds over Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>

The Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst was tested using all  $P_{CO}/P_{CO2}$  ratios excluding  $\infty$  using all other reaction conditions described in the methods. In this operating window a stable steady state performance of the catalyst was quickly achieved at all conditions and no deactivation effects were observed.

Figure 3a and b shows the performance of the different parallel beds under a reference condition (473 K, 25 bar). In Figure 3a, the  $P_{CO}/P_{CO2} = 10$  and  $CO_2$  consumption and  $H_2O$  production quickly flatten after the first sector, owing to the reverse water gas shift (RWGS) equilibrium being reached. Meanwhile in Figure 3b, this trend is very different. Water production only begins to slow at the back of the reactor. This is due to a shift in the RWGS equilibrium position due to the lower  $P_{CO}/P_{CO2}$  ratio of 1. Methanol production is similar in both examples although in the  $P_{CO}/P_{CO2} = 10$  system it is seen to accelerate slightly with axial distance, whilst the reverse is true for  $P_{CO}/P_{CO2} = 1$ . This trend is seen through the tested temperature range of 453 - 493 K.



Figure 3: Steady-state axial concentration plots for a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst operating at 473 K, 7.5 L h<sup>-1</sup> conditions with CO/CO<sub>2</sub> inlet ratios of A) 10:1 and B)
1:1. Symbols denote: (■) CO, (■) CO<sub>2</sub>, (■) CH<sub>3</sub>OH and (■) H<sub>2</sub>O. Lines are to guide the eye.

In all, 38 different reaction conditions were tested at steady state, giving 152 observations in total over the four parallel beds. Inspection of the position of RWGS equilibrium position at the inlets to all 4 catalyst bed sectors revealed that the data could be divided into two datasets for kinetic modeling purposes. 44 observations showed an inlet RWGS equilibrium term value of  $\beta_{RWGS} < 1$ , whilst 108 showed values of  $\beta_{RWGS} > 1$  and were hence in the forwards water gas shift (FWGS) regime.

The most successful model to describe both datasets was that of Vanden Bussche and Froment (1996). For both datasets, the impact of all possible surface species populations in the micro kinetic model on methanol synthesis and F/RWGS were considered. This includes formate, carbonate, hydrogen, water and hydroxyl populations. The final kinetic model descriptions are shown in Eq. (5) and (6):



$$r_{MeOH} = \frac{\dot{K}_{MeOH} P_{CO2} P_{H2} (1 - \beta_{CO2 -->MeOH})}{\left(1 + K_{redox} \frac{P_{H2O}}{P_{H2}} + K_{Carb} P_{CO2} P_{H2}\right)^3}$$
(5)

FWGS ( $\beta_{RWGS} > 1$ ) dataset:

$$r_{MeOH} = \frac{\dot{K_{MeOH}} P_{CO} P_{H2} (1 - \beta_{CO->MeOH})}{(1 + K_{Carb} P_{CO2} P_{H2})^3}$$
(6)

The value of the estimated parameters for both models is shown in Table 1:

Tuble 1. Estimated parameters in kinetic model					
Parameter	<b>RWGS dataset</b>	FWGS dataset			
А' <sub>МеОН,</sub> 473К	$0.48\pm0.12$	$0.10\pm0.01$			
Ea'MeOH	$76.3\pm9.0$	$81.4\pm4.6$			
Kredox	$76.5\pm48.0$	-			
<b>K</b> Carb	$0.07\pm0.03$	$0.014\pm0.01$			

 Table 1: Estimated parameters in kinetic model

The two separate models are necessary to describe the system as the FWGS position extends significantly into a kinetically relevant regime. Significantly, both models do not require a separate R/FWGS reaction term.

In the RWGS region this owes to the negligible presence of this reaction under the conditions explored. This is not surprising, as the activation energy for this reaction according to Vanden Bussche and Froment (1996) is high (~95 kJ mol<sup>-1</sup>) and the temperatures explored in this dataset are at the low end for methanol synthesis (453 - 493 K).

In the FWGS region, the reaction appears to be lumped into methanol synthesis reaction. In this dataset, CO rather than  $CO_2$  is the source of carbon for methanol however the activation energy for methanol synthesis is the same within confidence intervals as that for the RWGS region. This suggests that methanol synthesis follows the same mechanism in both regimes.

The FWGS mechanism over Cu in this model is redox based and involves the pickup of surface oxygen by CO. This suggests that the FWGS redox steps are an integrated part of the catalytic cycle in the FWGS dataset and is not rate determining, whilst this is not the case in the RWGS dataset. It also suggests that the CO<sub>2</sub> formed due to CO picking up surface oxygen remains adsorbed in these conditions and is converted through to methanol.

# Kinetics for CO/H<sub>2</sub> feeds – Functionality vs. Formulation

The performance of the three catalyst formulations was tested under both CO<sub>2</sub>-containing and CO<sub>2</sub>-absent conditions. Results are shown in Table 2:

Table 2: Steady state methanol observed in exit stream for different Cu-based formulations as  $f(P_{CO}/P_{CO2})$ 

ratio. 500 mg catalyst, 4/3 K, 25 bar					
Catalyst	$P_{CO}/P_{CO2} = 1$	$P_{CO}/P_{CO2} = \infty$			
	(µmol <sub>MeOH</sub> g <sup>-1</sup> s <sup>-1</sup> )	(µmol <sub>MeOH</sub> g <sup>-1</sup> s <sup>-1</sup> )			
Cu/ZnO/Al <sub>2</sub> O <sub>3</sub>	1.04	0.22			
Cu/ZnO	0.44	0.19			
Cu/Al <sub>2</sub> O <sub>3</sub>	0.06	0.00			

The methanol productivity of the materials largely follows the classic Cu surface area-activity relationship for  $P_{CO}/P_{CO2} = 1$ . This is not the case for

 $P_{CO}/P_{CO2} = \infty$ ; the ZnO containing catalysts are similar and the Cu/Al<sub>2</sub>O<sub>3</sub> sample produces no methanol at all.

The presentation will present detailed analysis of the behavior of these catalysts in  $CO/H_2$  feeds. Analysis of these catalysts is not possible by steady state means as the (ZnO containing) materials lose structural oxygen on a time dependent basis. The steady state functionality under  $CO/H_2$  of these catalysts changes as a function of conditions history (e.g. temperature during initial exposure). This was an observation made by Bos et al., (1989). Therefore to approach an understanding of this system under  $CO/H_2$ conditions, surface population balances and dynamic kinetic models are required.

#### Conclusions

This study has demonstrated the importance of considering catalyst formulation, reaction pathway functionality and active sites generation as a function of reaction conditions in tandem.

It has been shown that the same micro kineticbased model for methanol synthesis can be applied across a wide range of  $P_{CO}/P_{CO2}$  ratios, but not in a  $CO_2$ -*absent* feed. In the former scenario,  $P_{CO}/P_{CO2}$  ratio helps determine direction of RWGS or FWGS in the system and the source of carbon in methanol, but the mechanism does not change. In the latter, highly reducing CO/H<sub>2</sub> conditions result in a loss of oxygen from the reducible catalyst support. The presence of a reducible support is a necessary requirement to synthesise methanol in these feeds suggesting that Cu surface area is not an adequate descriptor alone for catalyst performance across the board.

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# STEADY-STATE AND TRANSIENT KINETIC STUDIES IN THE PALLADIUM CATALYZED ACETOXYLATION OF TOLUENE

Sven Reining, Evgenii V. Kondratenko<sup>\*</sup>, Narayana V. Kalevaru, Andreas Martin Leibniz-Institut für Katalyse, Albert-Einstein-Straße 29a 18059 Rostock, Germany

#### Abstract

The individual reaction steps of the acetoxylation of toluene to benzyl acetate were investigated over Pd-Sb/TiO<sub>2</sub> catalyst in a temperature range of 443-503 K by means of steady-state catalytic tests, steady-state isotopic transient kinetic analysis (SSITKA) and transient switch experiments. It was established that the main product benzyl acetate and side-product benzaldehyde are formed in parallel reactions from toluene. This aromatic compound is initially activated to yield an adsorbed benzyl cation that undergoes the desired acetoxylation and reacts with water to benzyl alcohol, which is further oxidized highly selective to benzaldehyde. Furthermore, transient and SSITKA experiments were performed to elucidate the role of gas-phase and lattice oxygen in toluene activation and in  $CO_2$  formation. Lattice oxygen was found to be responsible for the formation of water, while decarboxylation of acetic acid results in  $CO_2$ . In addition, in-situ temperature programmed oxidation (TPO) experiments revealed that carbon deposits are formed by decomposition of acetic acid and aromatic oxygenates are formed by consecutive oxidation of toluene.

#### Keywords

Steady-state isotopic transient kinetic analysis, transient response method, oxygen exchange, reaction kinetics.

#### Introduction

The acetoxylation of olefins is a well-known one-step reaction leading to acetates; in particular the gas-phase reaction of ethylene with acetic acid to vinyl acetate (VAM) over Pd-containing catalysts (Wackerprocess) is an outstanding example of large-scale acetoxylation (Bauer et al., 1988). This reaction product is an important monomer widely used in the polymer industries. Due to its industrial relevance, the kinetics and the mechanism of the VAM synthesis have been already investigated by several research groups using various experimental (Han et al., 2005; Motahari et al., 2012) and theoretical (Gao et al., 2008; Hansen et al., 1994; Plata et al., 2009; Stacchiola et al., 2005) approaches. In general, it is accepted that the acetoxylation of ethylene includes a ß-hydride elimination step, which is known as Samanos pathway (Samanos et al., 1971; Stacchiola et al., 2005). In a similar way, aromatic compounds can be used as reactants for acetoxylation reactions to vield

corresponding esters. For example, we have demonstrated (Benhmid et al., 2005a) the feasibility of gas-phase acetoxylation of toluene to benzyl acetate (see Figure 1), which is widely used in perfumery, food, and chemical industries.



Figure 1. Acetoxylation of toluene

This reaction is also a good example for the so-called "Green Chemistry" since it opens a new and chlorinefree way and thus, environmental friendly route for the large-scale production of benzyl alcohol through simple hydrolysis of benzyl acetate. The acetoxylation of toluene is catalyzed by Pd-Sb/TiO<sub>2</sub> with high activity and selectivity above 85% at the toluene conversion of 92% (Benhmid et al., 2005b). Benzaldehyde was the main side-product, while small amounts of CO<sub>2</sub> and benzyl alcohol were also observed.

However, individual reaction steps leading to desired and side-products have not been thoroughly elucidated yet. In order to close this gap, a series of steady-state and transient experiments was carried out in the present study with the purpose of determining overall scheme of toluene acetoxylation and also to derive mechanistic insights into products formation. Furthermore, the experiments were also kinetically evaluated.

<sup>\*</sup>evgenii.kondratenko@catalysis.de

#### Experimental

A catalyst with a nominal content of 10 wt.-% Pd-16 wt.-% Sb/TiO<sub>2</sub> was used in all the experiments. It was prepared by wet impregnation method in a two-step procedure. Details about the catalyst preparation were already published (Gatla et al., 2011). Steady-state and transient experiments were performed in in-house developed set-ups as described below.

#### Steady-state experiments

Catalytic tests were performed in a fixed-bed continuous flow tubular reactor ( $\emptyset_{inner} = 9.4 \text{ mm}$ ) made of Hastelloy C. Gaseous and liquid (toluene and acetic acid) feed components were dosed by mass flow controllers and HPLC-pump, respectively. Before entering the reactor, the liquids were vaporized and mixed with the gas-phase components. The catalyst (0.4-0.6 mm particles) was diluted by the fourfold amount of corundum particles to maintain isothermal conditions. A reactant mixture of toluene/acetic  $acid/O_2/Ne+CH_4 = 1/4/3/17$  was used. Thereby, methane (5 vol.-% in Ne) was introduced as internal standard. The temperature was varied from 443-483 K and a pressure of 2 bar was adjusted. To determine the selectivity-conversion relationship, catalytic tests were performed at different contact times achieved through variation of the amount of catalyst (0.2-1.2 g) while the total reactants flow was held constant (120 mmol/h).

Internal and external mass transport limitations can be neglected. This was proven by performing tests with different sieve fractions of the catalyst to check whether internal limitations and varying the amount of catalyst and the total flow so that the contact time remained constant to check whether external limitations occur.

Furthermore, to identify possible reaction intermediates in the benzyl acetate synthesis, we also carried out tests using a reaction feed of either benzyl alcohol or benzaldehyde instead of toluene.

The feed components and the reaction products were analyzed by an on-line gas chromatograph (Shimadzu) equipped with flame ionization and thermal conductivity detectors.

#### Transient experiments

The transient experiments were performed in an inhouse developed set-up equipped with an on-line quadrupole mass spectrometer (QMS, Pfeiffer Vacuum OmniStar 200) to properly record fast changes in the concentration of feed components and reaction products. Additionally, a pressure driven valve is installed which can switch between two reaction mixtures in a millisecond regime and thus, it is suitable for performing transient experiments. 0.2 g or 0.4 g (in the SSITKA experiments) catalyst particles (0.2-0.4 mm) diluted by the threefold amount of corundum particles was loaded into a quartz tube reactor ( $\emptyset_{inner} = 6$  mm).

A temperature of 483 K and a pressure of 2 bar were adjusted in all the transient experiments. A step input of the reaction mixture from inert flow was performed and the transient responses of the reactants and products were collected by QMS. When reaching the new steady-state, a switch from the reaction mixture to inert flow was performed.

Steady-state isotopic transient kinetic analysis (SSITKA) was performed additionally (Shannon and Goodwin, 1995). Therefore, two reaction mixtures with identical concentrations were prepared, i.e. toluene/O<sub>2</sub>/acetic acid/inert = 1/3/4/17; but one contained <sup>16</sup>O<sub>2</sub> oxygen and the second one <sup>18</sup>O<sub>2</sub>. After reaching the steady-state using the feed with non-labeled oxygen (<sup>16</sup>O<sub>2</sub>), a switch between both the reaction mixtures was carried out.

In an additional experiment, not only the isotope of oxygen was exchanged but also the oxygen was replaced from the reaction feed by inert.

Furthermore, in-situ temperature programmed oxidation (TPO) experiments were performed after treating the catalyst at different reaction temperatures (463-503 K) and under different feed compositions, i.e. acetic acid/ $O_2$ , toluene/ $O_2$ , and toluene/acetic acid/ $O_2$ .

#### **Results and discussion**

#### Steady-state experiments

The steady-state experiments revealed that benzyl acetate and benzaldehyde are formed in parallel since the selectivity to both these products does not depend on the conversion of toluene. When dosing benzaldehyde instead of toluene, no conversion could be obtained until a reaction temperature of 483 K which is in accordance with the above selectivityconversion relationship.

An interesting result was obtained when benzyl alcohol instead of toluene was used as feed. Benzaldehyde was the main reaction product, while benzyl acetate was formed with very low selectivity even at a conversion above 90 %. The formation of benzyl acetate proceeds in this case probably via the elimination of water from benzyl alcohol followed by addition of acetate. Hence, benzyl alcohol is not an intermediate in the formation of benzyl acetate which is in contrast to the typical esterification in the liquid phase; but it is probably a short-lived intermediate in the formation of benzaldehyde.

The data obtained from the experiments varying the modified residence time at three different temperatures (443, 463, and 483 K) were treated in a certain way to determine the activation energies of the formation of benzyl acetate and benzaldehyde. First of all, their yields were calculated from each experimental run. The

yield of benzyl acetate as a function of the modified residence time is shown in Figure 2.



Figure 2. Yield of benzyl acetate as a function of the modified residence time at different temperatures,

#### 483 $K(\Delta)$ , 463 $K(\bigcirc)$ , and 443 $K(\bigcirc)$

As expected, the yield increases with the residence time and with the temperature. Similar results were obtained for the yield of benzaldehyde (see Figure 3). For the further kinetic evaluation, the data were fitted with a polynomial function of second order to obtain the initial reaction rate by the derivative. Thereby, the goodness of fit was in every case > 99 %.



Figure 3. Yield of benzaldehyde as a function of the modified residence time at different temperatures,

483 K (
$$\Delta$$
), 463 K ( $\bigcirc$ ), and 443 K ( $\_$ 

The logarithm of the reaction rate was plotted against 1/T to determine the apparent activation energies for the formation of benzyl acetate and benzaldehyde.

The Arrhenius plot resulted in a straight line and the goodness of fit was in both the cases > 97 %.

As a result, the apparent activation energies of  $25.4 \text{ kJ mol}^{-1}$  for the formation of benzyl acetate and  $25.6 \text{ kJ mol}^{-1}$  for the formation of benzaldehyde were obtained.

It is interesting to note that the activation barriers have the same value within an experimental error. The similar activation energies indicate that the activation of toluene, i.e. the hydrogen abstraction to yield adsorbed benzyl cation, may be the rate-limiting step since this intermediate is involved in the formation of benzyl acetate and benzaldehyde. Thus, the availability of the respective coupling molecule, i.e. acetate or hydroxyl group, probably controls the selectivity to the corresponding reaction products. The optimization of the reaction conditions revealed an ideal molar ratio of toluene/acetic acid = 1/4 (Madaan et al., 2011). This result indicates that an excess of acetic acid in the feed leads to a high selectivity to benzyl acetate which underlines the assumption mentioned above.

#### Transient experiments

The goal of the transient experiments was to elucidate the role of gas-phase and lattice oxygen in the toluene acetoxylation. The transient responses of O2 and the reaction products benzyl acetate, CO<sub>2</sub>, and H<sub>2</sub>O after switching from the reaction mixture to inert flow are shown in Figure 4. The profile of H<sub>2</sub>O shows an overshoot in presence of inert flow. This indicates a faster desorption compared to the steady-state. Furthermore, the O<sub>2</sub> profile overlaps with the H<sub>2</sub>O and benzyl acetate profiles in one point, respectively. Thus, H<sub>2</sub>O and small amounts of benzyl acetate are formed even in the absence of gas phase O<sub>2</sub>. An integration of the transients from 43 s to 150 s revealed the amount of produced H<sub>2</sub>O and available gas phase O<sub>2</sub>. Taking into account an O<sub>2</sub> conversion of 5 % known from the GC measurement in the steady-state, a comparison of the converted O<sub>2</sub> and the amount of formed H<sub>2</sub>O in the mentioned time span revealed that more H<sub>2</sub>O was formed as gas-phase O2 was converted. This result indicates that oxygen species from the catalyst probably take part in the reaction.

The participation of lattice oxygen was also demonstrated in the transient experiment when gasphase  $O_2$  was replaced by an inert gas in the reaction mixture. It was found that  $H_2O$  was still formed in the absence of gas-phase  $O_2$ .

The formation of  $CO_2$  was investigated in the SSITKA experiment. No  $C^{18}O_2$  could be observed even after a certain period of time which indicates the formation of  $CO_2$  by decomposition of acetic acid as single remaining source of <sup>16</sup>O.



Figure 4. Transient responses after switching from the reaction mixture to inert flow, 483 K, 2 bar

In-situ TPO experiments were performed to elucidate the origins of surface carbon containing species formed during the acetoxylation reaction and thus to gain deeper insights and comprehensive knowledge about the complete reaction network.

The TPO profiles after treating the catalyst under reaction feed with a molar concentration of toluene/acetic acid/O<sub>2</sub>/inert = 1/4/3/17 show two types of surface carbon species as concluded from the fact that two maxima of CO<sub>2</sub> evolution were observed at approximately 528 K and 613 K.

When the acetoxylation reaction was performed at 503 K, the first maximum disappeared. Based on the results obtained we put forward that the first maximum of  $CO_2$  evolution belongs to decarboxylation of acetic acid and the second one to the total oxidation of the aromatic ring.

#### Conclusions

The acetoxylation of toluene was investigated over Pd-Sb/TiO<sub>2</sub> catalyst in steady-state and transient experiments. It was found that benzyl acetate and benzaldehyde as main side-product are formed in parallel reaction pathways. These products are probably formed from a benzyl cation through either desired acetoxylation or undesired hydroxylation. Benzyl alcohol formed in the latter reaction is easily oxidized to benzaldehyde. Furthermore, decarboxylation of acetic acid takes place forming  $CO_2$  and surface coke which is responsible for deactivation of the catalyst.

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# A SINGLE-EVENT MICROKINETIC MODEL FOR THE COBALT CATALYZED FISCHER-TROPSCH SYNTHESIS

Jonas Van Belleghem<sup>a</sup>, Joris W. Thybaut<sup>a,\*</sup>, De Chen<sup>b</sup> and Guy B. Marin<sup>a</sup> <sup>a</sup> Ghent University, Laboratory for Chemical Technology, Technologiepark 914 Ghent B-9052 Belgium

<sup>b</sup> Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), 7491 Trondheim,

Norway

#### Abstract

A Single-Event MicroKinetic model has been validated for the Fischer-Tropsch synthesis on a cobalt based catalyst. The experiments were performed in a plug flow reactor with a  $H_2$  to CO molar inlet ratio between 5 and 10, a temperature range from 483 K – 503 K and CO partial pressures from 3.7 kPa to 7.5 kPa. The microkinetic model is based on the carbene insertion mechanism and all the reactions are considered reversible. The UBI-QEP method was used to calculate the chemisorption enthalpies of the surface species. Via regression, statistically significant and physicochemically meaningful values for the adjustable model parameters, i.e., the activation energies of the considered elementary steps and atomic chemisorption enthalpies of H, C and O were obtained. The incorporation of symmetry numbers together with a stronger chemisorption enthalpy of the metal methyl species were found to be two crucial aspects to explain the typical deviations from the Anderson-Schulz-Flory distribution.

#### Keywords

Fischer-Tropsch Synthesis, Single-Event MicroKinetics (SEMK), UBI-QEP.

#### Introduction

Fischer-Tropsch Synthesis (FTS) has experienced a strong resurgence during the last decades. Fe, and more recently, Co based catalysts are typically employed. The higher Fischer-Tropsch reaction rate, lower watergas shift activity and slower deactivation make the Co catalyst the preferred one, particularly when methane is used as source for the syngas production.

While a wide variety of kinetic models exists for simulating Fischer-Tropsch synthesis, the number of those models that is able to describe the product distribution in detail for the Co catalyzed FTS is limited (Todic et al., 2014). One of the main challenges in constructing such models is to adequately capture deviations from the Anderson-Schulz-Flory (ASF) distribution, e.g., the higher methane selectivity and lower ethene selectivity than expected from this distribution, while keeping the number of adjustable parameters in the model within manageable limits. Furthermore, most of these kinetic models are based on a priori assumptions about rate determining steps (Bhatelia et al., 2014; Todic et al., 2014).

In this work, a previously developed Single-Event MicroKinetic (SEMK) model for the Fe based FTS (Lozano-Blanco et al., 2008) is used. The number of single events, as calculated in the SEMK model, was found to be of primordial importance to explain the deviations from this ASF distribution. It is noted that in this model, all the elementary reactions are considered reversible while none of them is considered quasi-equilibrated.

#### **Experimental Procedures**

A 20 wt% Co on carbon nanotubes (Co/CNT) catalyst has been investigated. The catalyst was activated as described by Yang et al (2013). The Co particles had an average diameter of 12.5 nm (Yang et al., 2013). This is considered large enough not to have any significant metal particle size effect on the catalyst activity and selectivity (den Breejen et al., 2009).

The experiments were performed in a SSITKA setup (Froseth et al., 2005). A CO inlet partial pressure ranging from 3.7 kPa to 7.5 kPa was used with H<sub>2</sub> to CO molar inlet ratios between 5 and 10 in a temperature range from 483 K to 503 K. In total 50 experiments were acquired out of which 41 were measured at different reaction conditions. The replicate experiments were used to estimate the experimental error.

#### **Modeling Procedures**

#### Reactor Model

The reactor is modeled as an ideal plug flow reactor. The variation in the reactant and product flow rates is, hence, described by Eq. (1). The pseudo-steady state approximation, Eq. (2), is applied for the surface species.

$$\frac{dF_i}{dW} = R_i \qquad \qquad i = 1, \dots, n_{gas} \tag{1}$$

$$=0 j=1,\dots,n_{surf} (2)$$

 $R_i$ 

<sup>\*</sup> To whom all correspondence should be addressed. Postal address: Ghent University, Laboratory for Chemical Technology, Technologiepark 914, B-9052 Gent, Belgium. E-mail address: Joris.Thybaut@UGent.Be

Where  $F_i$  is the molar flow rate of component i [mol /s], W the catalyst mass [kg],  $R_i$  the net production rate of species i [mol/(kg<sub>cat</sub> s)].

#### Reaction Mechanism and Rates

The carbene insertion mechanism is considered in this work, see Table 1. Adsorbed CO is assumed to dissociate to surface carbon, C, and oxygen, O. This surface carbon is hydrogenated to  $CH_2$  which acts as the monomeric building block. The growing alkyl chain can undergo hydrogenation to the corresponding alkane or dehydrogenate to a metal alkene which can subsequently be desorbed as an alkene. The surface oxygen is removed via two consecutive hydrogenations resulting in water.

#### Table 1: Elementary steps considered in the reaction network together with the adjustable model parameters.

Reaction	Adjustable
	Model Parameter
$H_2 + 2^* \leftrightarrow 2H^*$	-
$CO +^{**} \leftrightarrow CO^{**}$	-
$CO^{**} + 3^* \leftrightarrow C^{***} + O^{**}$	$E_{a,1}$
$C^{***} + H^* \leftrightarrow CH^{***} +^*$	$E_{a,2}$
$CH^{***} + H^* \leftrightarrow CH_2^{**} + 2^{**}$	E <sub>a,3</sub>
$CH_2^{**} + H^* \leftrightarrow CH_3^* +^{**}$	E <sub>a,4</sub>
$C_n H_{2n+1}^* + C H_2^{**} \leftrightarrow C_{n+1} H_{2n+3}^* + **$	E <sub>a,5</sub>
$C_n H_{2n+1}^* + H^* \leftrightarrow C_n H_{2n+2}$	E <sub>a,6</sub>
$C_n H_{2n+1}^* +^* \leftrightarrow C_n H_{2n}^* + H^*$	Ea,7
$C_n H_{2n}^* \leftrightarrow C_n H_{2n} +^*$	-
$O^{**} + H^* \leftrightarrow OH^* + 2^{**}$	E <sub>a,8</sub>
$OH^* + H^* \leftrightarrow H_2O + 2^{**}$	E <sub>a,9</sub>

While forward activation energies constitute the set of adjustable model parameters, the reverse activation energies are calculated based on thermodynamic consistency. The correspondingly required standard reaction enthalpies of the surface reactions are obtained via a Born-Haber cycle in which also the standard reaction enthalpies of the corresponding gas phase reactions and the chemisorption enthalpies of the surface species are involved. The chemisorption enthalpies of the various species in the reaction network are calculated using the UBI-QEP method (Lozano-Blanco et al., 2008; Shustorovich & Sellers, 1998). This methodology only requires three adjustable parameters, i.e., the atomic chemisorption enthalpy of H, C and O.

The rate coefficients are expressed making use of the Single-Event MicroKinetic (SEMK) methodology (Lozano-Blanco et al., 2008), see Eq. (3).

$$k = \frac{\sigma_{gl,r}}{\sigma_{gl,\neq}} \tilde{A} \exp\left(-\frac{E_a}{RT}\right)$$
(3)

Where  $\sigma_{gl,r}$  and  $\sigma_{gl,\neq}$  are the global symmetry numbers of the reactant and transition state,  $\tilde{A}$  the single-event pre-exponential factor [1/s or 1/(Pa s)],  $E_a$  the activation energy [kJ/mol], R the universal gas constant [J/(mol K)] and T the temperature [K].

The pre-exponential factor is calculated using the Sackur-Tetrode equation (Atkins & De Paula, 2006) and by making reasonable assumptions with respect to the number of translational degrees of freedom lost or gained during transition state formation (Dumesic et al., 1993).

The reaction network corresponding to the mechanism displayed in Table 1 has been generated using ReNGeP (Lozano-Blanco et al., 2006).

#### Regression

Values for the adjustable parameters in the SEMK model, i.e., the activation energies listed in Table 1 and the atomic chemisorption enthalpies are obtained by minimizing the following objective function:

$$\sum_{i=1}^{n_{exp}} \sum_{j=1}^{n_{res}} w_{i,j} \left( F_{i,j} - \hat{F}_{i,j} \right)^2 \xrightarrow{E_a.Q} Min \tag{4}$$

Where  $n_{exp}$  represents the number of experiments,  $n_{res}$  the number of responses in experiment i,  $w_{i,j}$  the weight of the j<sup>th</sup> response in the i<sup>th</sup> experiment,  $F_{i,j}$  the j<sup>th</sup> observed response in the i<sup>th</sup> experiment and  $\hat{F}_{i,j}$  the calculated response.

#### **Results and Discussion**

#### Experimental Observations

The temperature effect on the CO conversion and alkanes and alkenes selectivity is displayed in Figure 1. The temperature was found to have a pronounced effect on the CO conversion with a corresponding apparent activation energy of 115 kJ/mol. The methane selectivity increases with the temperature, while the selectivity to the other alkanes decreases. The ethene selectivity is constant as a function of temperature, while the propene selectivity exhibits a decreasing trend with the temperature.

The effect of the  $H_2$  to CO molar inlet ratio on the CO conversion and product selectivity was also investigated. The CO conversion was found to increase with an increasing  $H_2$  to CO molar inlet ratio, while product selectivities only varied within the experimental error.



Figure 1: The effect of temperature on the CO conversion ( $\blacksquare$ :483K;  $\blacklozenge$ :493K and  $\blacktriangle$ :503K -left) and alkanes ( $\blacksquare$ :CH<sub>4</sub>;  $\blacklozenge$ : C<sub>2</sub>H<sub>6</sub>;  $\blacktriangle$ :C<sub>3</sub>H<sub>8</sub>;  $\diamond$ :C<sub>4</sub>H<sub>10</sub> and  $\triangle$ :C<sub>5</sub>H<sub>12</sub> - middle) and alkenes ( $\blacklozenge$ :C<sub>2</sub>H<sub>4</sub> and  $\blacksquare$ :C<sub>3</sub>H<sub>6</sub> - right) selectivity. The effect of temperature on the selectivities is presented for points close to isoconversion. The symbols are the experimental measurements, the lines are simulated with the microkinetic model. The other experimental conditions were a H<sub>2</sub> to CO molar inlet ratio of 10, a CO inlet partial pressure equal to 5.5 kPa and a total pressure of 1.85 kPa. The error bars indicate  $\pm \sigma$ .

#### Parameter Estimation

The regression results are summarized in Table 2. All the parameters are estimated significantly as none of the individual 95% confidence intervals includes zero. The F value for the global significance of the regression amounts to 620 which is considerably higher than the tabulated value, i.e., 2.79.

Table 2: Results of the parameter estimation

Parameter	Value [kJ/mol]
E <sub>a,1</sub>	$45.8 \pm < 0.1$
E <sub>a,2</sub>	$65.7 \pm 19.4$
E <sub>a,3</sub>	$10.1 \pm 3.0$
$E_{a,4}$	$72.8 \pm 0.6$
$E_{a,5}$	$35.8\pm0.7$
$E_{a,6}$	$90.6 \pm < 0.1$
Ea,7	$66.2 \pm 0.2$
$E_{a,8}$	$107.0 \pm 2.5$
Ea,9	$100.3 \pm 3.6$
Q <sub>H</sub>	$-256.0 \pm 0.1$
Q <sub>C</sub>	$-657.7\pm0.4$
Qo	$-564.3 \pm 0.3$

The estimates are in line with the general, physicochemical constraints such as positive activation energies and negative chemisorption enthalpies.

The H atomic chemisorption enthalpy is in correspondence with ab initio (Gong et al., 2004), -259 kJ/mol, and experimental values (Benziger, 1992), -251kJ/mol. The atomic chemisorption enthalpy of C is in between the ab initio calculated value (Gong et al., 2004), -657.7 kJ/mol, and the experimentally determined one of -678 kJ/mol (Benziger, 1992). The O atomic chemisorption enthalpy exceeds the ab initio reported value (Gong et al., 2004) and experimentally determined one (Benziger, 1992) by more than 50 kJ/mol.

The UBI-QEP method results in an adsorption enthalpy for the methyl radical of -229.5 kJ/mol

and -187 kJ/mol for the heavier alkyl radicals. The stronger adsorption of the methyl radical was obtained by describing the adsorption as a superposition of strong and intermediate adsorption strength within the UBI-OEP framework. The stronger adsorption of the methyl radical was found to be a key feature required for the adequate simulation of the methane yield. The stronger chemisorption for the methyl radical compared to the heavier alkyl radicals is also obtained from ab initio calculations (Cheng et al., 2008a). A CO adsorption enthalpy of -118 kJ/mol was obtained. This value is in between the experimentally determined value (Bridge et al., 1977) and the ab initio reported one (Gong et al., 2004). Other kinetic modeling studies report values between -48.9 kJ/mol (Todic et al., 2014) and -86.7 kJ/mol (Azadi et al., 2015). The alkene chemisorption enthalpies vary between -63.8 kJ/mol and -66.5 kJ/mol. These values are less negative than the ab initio calculated values, i.e., -75 kJ/mol (Cheng et al., 2008a). Alkene adsorption was only considered as an elementary step in one other model (Azadi et al., 2015). These authors considered the possibility of activated desorption in their model and distinguished between the chemisorption of ethene, propene and higher alkenes. This resulted in chemisorption enthalpies varying from -120 kJ/mol for ethene to +43 kJ/mol for the higher alkenes.

The trend in the activation energies for the monomer formation is the same as has been found for an Fe catalyst (Lozano-Blanco et al., 2008). The activation energy for methylene insertion,  $E_{a,5}$ , is lower than the activation energy found by (Azadi et al., 2015), i.e., 35.8 kJ/mol compared to 39.5 kJ/mol to 57.3 kJ/mol. The activation energy for the alkane formation exceeds that for metal alkenes formation. This trend is confirmed by another kinetic modeling study (Azadi et al., 2015) as well as by ab initio calculations (Cheng et al., 2008b). The value for the metal alkyl hydrogenation is lower than the one reported by Azadi (2015). The activation energy for the metal alkenes formation is much closer to the value reported by Azadi (2015) for the higher alkenes (n>3).

The model performance is presented in Figure 1. The model is capable to reproduce the experimental data for all the observed components. Only propene seems to be slightly overestimated by the model.

#### Explanation of the Observed Trends

The high methane selectivity is attributed to the higher stability on the surface of the metal methyl species. Another factor which increases the methane selectivity is the number of single events. This increases the hydrogenation rate of the metal methyl species with a factor 3 compared to the other metal alkyl species.

The low ethene selectivity can also be attributed to the difference in symmetry numbers. The readsorption rate of ethene exceeds that of the other 1-alkenes by a factor of 2.

In accordance with the Arrhenius relationship, reaction rates increase exponentially with the temperature. An increasing temperature will, hence, increase the desorption rate freeing up free sites which are essential for the CO dissociation. This increases the CO dissociation rate and, thus, increases the CO conversion.

The increasing methane selectivity with increasing temperature can be explained by the activation energy for methylene hydrogenation,  $E_{a,4}$ , and that of metal alkyl hydrogenation,  $E_{a,6}$ . Both activation energies are among the highest activation energies in the reaction network. Increasing temperatures will selectively increase the rates of these reactions and, hence, the methane selectivity. This is accompanied by a decreasing selectivity to the other alkanes as less methylene species will be present on the surface for chain growth.

#### Conclusions

A detailed Single-Event MicroKinetic model has been validated for a Co based catalyst. The model is based on the carbene insertion mechanism and each elementary step is considered reversible. All the parameters in the model could be estimated significantly. The use of symmetry numbers together with a stronger chemisorption enthalpy of the metal alkyl species were found to be crucial aspects to explain the typical deviations from the Anderson-Schulz-Flory distribution.

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# Study of gas-liquid photocatalytic kinetics via a compact photomicroreactor assembly

Yuanhai Su<sup>\*</sup>, Volker Hessel and Timothy Noël<sup>\*</sup>

Micro Flow Chemistry and Process Technology, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Den Dolech 2, 5600 MB Eindhoven, The Netherlands

#### Abstract

A compact photomicroreactor assembly that consisted of a capillary microreactor and small-scale light emitting diodes (LEDs) was developed for the study of reaction kinetics in the gas-liquid photocatalytic oxidation of thiophenol to phenyl disulfide within Taylor flow. The importance of photons for this process was convincingly shown by observation of a suction phenomenon due to the fast consumption of oxygen. Mass transfer limitations in the photocatalytic process were evaluated and an operational zone without mass transfer effects was chosen to study reaction kinetics. The effects of photocatalyst loading and light sources on the reaction performance were investigated. Reaction kinetic analysis was performed, and the reaction orders with respect to both thiophenol and oxygen were deduced based on heterogeneous and homogeneous experimental results, respectively. Based on the measured reaction rate constants, the Hatta number could be calculated which further indicated mass transfer limitations could be overcome by using a photomicroreactor. The reaction rate constants at different photocatalyst loadings and different photon flux were also calculated. In addition, the reaction rate constants obtained in the photomicroreactor assembly and in a batch reactor were compared, which demonstrated the advantages of this photochemical column for the study of reaction kinetics in gas-liquid photocatalytic processes.

#### Keywords

reaction kinetics, microreactors, photocatalysis, disulfides, aerobic oxidation, mass transfer.

#### Introduction

Photochemical transformations are commonly used in the fields of organic synthesis, material science and environmental treatment.<sup>1</sup> In these applications, photons are utilized to provide sufficient energy to overcome the activation barrier. Light activation provides remarkable pathways for many kinds of reactions, which are difficult or impossible to reach via thermochemical activation. Recently, the use of visible light photoredox catalysis has become very popular in organic synthetic chemistry as it allows to perform chemical reactions under mild reaction conditions. In this activation mode, organometallic complexes<sup>2</sup> or organic dyes<sup>3</sup> are often applied to absorb photons and to engage in single electron or energy transfer processes with organic substrates.

Conventional reactors such as immersion-well photoreactors in conjunction with mercury-vapor discharge lamps are widely used for UV photochemical transformations in organic synthetic laboratories.<sup>4</sup> However, it is difficult to reach a homogeneous irradiation inside these batch reactors due to their large characteristic dimensions. This photon maldistribution originates from long transport distance according to the Lambert-Beer law.<sup>5</sup> Moreover, the effective contact area and the mass transfer rate in batch reactors are usually insufficient especially for fast photochemical reactions. This makes the scale-up of batch reactors via a dimension enlarging approach very challenging.

• Tel.: +31402473623, E-mail address: <u>t.noel@tue.nl;</u> y.su@tue.nl.

To generate new, efficient photocatalysts and optimized chemical formulations, reaction mechanisms and their kinetic characteristics should be understood. In the past decade, microreactor technology has received increasing attention in the study of reaction kinetics, due to its excellent transport properties compared to batch reactors.<sup>6</sup> In particular, extremely small characteristic dimensions of microreactors ensure excellent light irradiation of the entire reaction medium and thus increase radiation homogeneity, showing great application potential on the photochemical transformations.<sup>7</sup> However, the application of microreactor technology for studying the kinetics of photochemical processes has not been performed yet.

In this work. we developed a compact photomicroreactor assembly that consisted of a capillary microreactor and small-scale light emitting diodes (LEDs) for the study of reaction kinetics in the gas-liquid photocatalytic oxidation of thiophenol to phenyl disulfide within Taylor flow.<sup>8</sup> The metal-free photocatalytic aerobic oxidation of thiophenol to phenyl disulfide under visible light illumination was chosen as a model reaction. In this photocatalytic process, Eosin Y and tetramethylethylenediamine (TMEDA) were used as a metal-free photocatalyst and a base, respectively. Mass transfer limitations were evaluated in order to get intrinsic kinetic data. The effects of photocatalyst concentration and LED light sources on the photocatalytic performance were studied without mass transfer limitations. Reaction kinetic analysis was conducted to obtain the reaction orders with respect to both thiophenol and oxygen. The reaction rate constants at different photocatalyst loadings and different photon flux were calculated. Furthermore, the reaction rate constants obtained in the capillary microreactor were compared with those obtained in a batch reactor.

#### **Experimental section**

Photomicroreactor design: A transparent capillary made of high purity perfluoroalkoxy alkane (PFA, IDEX Health and Science; ID: 750 µm; length: 2.15 m; volume: 0.95 ml), a commercial light stripe with smallscale LEDs (Paulmann Lighting GmbH) and two plastic syringes were used to construct the compact photomicroreactor assembly (photochemical column), as shown in Figure 1. A LED stripe was coiled around the inner wall of a larger plastic syringe (100 ml), with all LED pillars (3 mm width and 2.5 mm height for each pillar) facing toward the central axis of this syringe. The syringe coiled with the capillary was fixed inside a larger diameter syringe. Light sources 1-3 were applied in this photocatalytic process. Pressurized air was supplied through the nozzle of the larger syringe in order to keep the whole system at room temperature.



Figure 1. Photomicroreactor design: (a) Different components of the photomicroreactor assembly, with (from left to right) the capillary microreactor coiled around an aluminum coated syringe, the LED stripe, and the outer syringe in which the photomicroreactor and LEDs are placed; (b) Assembled version; (c) Photomicroreactor assembly in operation.

Experimental procedure: The substrate solution (0.5 M thiophenol in ethanol) and the catalyst solution (Eosin Y and TMEDA in ethanol) were introduced into the system by two syringe pumps (Fusion 200 Classic), merged in a T-micromixer. The reaction mixture was then delivered to a second T-micromixer and contacted with oxygen controlled by a gas mass flow controller (Bronkhorst). A Taylor flow regime was established, and then flowed through the capillary microreactor in the small photochemical column. The pressure drop in the capillary microreactor could be measured via a pressure transducer (Huba Control) prior to the gas phase inlet of the second T-micromixer, which was used to calculate the residence time (t) of the gas-liquid two phases. Saturated aqueous ammonium chloride solution and ethyl acetate were fed to a third Tmicromixer and contacted with the gas-liquid biphasic stream from the photochemical column in order to completely quench the reactions after exiting the capillary microreactor. A small vial was used to collect the reaction mixture. The organic phase in the vial was collected and analyzed by GC FID in order to obtain the product yield.

#### **Results and discussion**

#### Evaluation of mass transfer limitation

When the volumetric flow rate ratio of gas to liquid phase reached 2, the mass transfer limitation of oxygen could be totally eliminated at high flow rates (i.e. short residence times). As shown in Figure 2, the yield did not depend on the volumetric flow rate ratio when the residence time was less than 100 s. The residence time was calculated based on Equation 1. The oxygen consumption and the pressure drop across the capillary microreactor in the photochemical column were considered in this equation.

$$t = \frac{V_c}{Q_G + Q_L} = \frac{V_c}{\frac{Q_{G,in} + Q_{G,out}}{2} \times \frac{P_{out}}{(P_{in} + P_{out})/2} + Q_L}}$$
$$= \frac{V_c}{\frac{Q_{G,in} + (Q_{G,in} - 0.25Q_LC_{sub,0}RTY/P_{out})}{2} \times \frac{P_{out}}{(P_{in} + P_{out})/2} + Q_L}}{(1)}$$

The operational zone without the mass transfer limitation (cf., Zone 1 in Figure 2) and the volumetric flow rate of gas to liquid phase of 3 were chosen in the following study of reaction kinetics.



Figure 2. Relationship between the yield and the residence time at two different volumetric flow rate ratios of gas phase to liquid phase (condition: 1 mol% Eosin Y loading, 1 equivalent TMEDA and light source 1).

#### Gas-liquid photocatalytic reaction kinetic analysis

Integration method was applied to deal with experimental data when studying reaction kinetics. Within Zone 1 in Figure 2, the oxygen concentration in the reaction mixture approximately maintained the same value and was equal to the saturated concentration of oxygen in ethanol, due to the fast mass transfer rate provided by the capillary microreactor. We made two assumptions, including the first order reaction and the second order reaction with respect to the substrate, when applying the integration method. If the photocatalytic reaction is first order with respect to thiophenol (case 1), the reaction rate of substrate can be expressed as follows:

$$r_{sub} = -\frac{dC_{sub}}{dt} = K_{sub,1}C_{sub}$$
(2)

$$\ln(\frac{C_{sub,0}}{C_{sub}}) = \ln(\frac{C_{sub,0}}{C_{sub,0}(1-X_{sub})}) = \ln(\frac{C_{sub,0}}{C_{sub,0}(1-Y)}) = K_{sub,1}t$$
(3)

where  $K_{sub,1}$  is the apparent reaction rate constant with regard to thiophenol in case 1. The value of  $K_{sub,1}$ includes information on the intrinsic reaction rate constant, the concentration of oxygen in the bulk liquid phase and the LED illumination. The yield (*Y*) is equal to the conversion ( $X_{sub}$ ) due to the fact that the selectivity of phenyl disulfide is 100%. We observed no overoxidation, which demonstrates the mildness of this photocatalytic protocol. If the reaction is second order with respect to the substrate (case 2), the reaction rate is given by the following equations:

$$r_{sub} = -\frac{dC_{sub}}{dt} = K_{sub,2}C_{sub}^2$$
(4)

$$\frac{1}{C_{sub,0}(1-Y)} - \frac{1}{C_{sub,0}} = K_{sub,2}t$$
(5)

where  $K_{sub,2}$  is the apparent reaction rate constant with regard to thiophenol in case 2. Figure 3 shows the validation of case 1. It can be seen that the experimental data can be well explained based on the assumption of case 1; the linear correlation coefficient for the relationship between  $\ln(C_{sub,0} / C_{sub})$  and the reaction time (residence time) is more than 0.99. However, the experimental data cannot be elaborated with the assumption of case 2. Based on this fundamental analysis, it can be concluded that the photocatalytic aerobic oxidation of thiophenol to phenyl disulfide is first order with respect to thiophenol.



Figure 3. Validation of the reaction order with respect to the substrate in the gas-liquid photochemical catalysis (1mol% Eosin Y loading, 1 equivalent TMEDA and light source 1) for case 1 with a first order assumption.

Furthermore, the reaction order with respect to oxygen was obtained. Minor variations on the experimental procedure were made in order to keep the conversion of thiophenol low and thus its concentration close to a constant value. We purged the substrate solution and/or the catalyst solution with pure oxygen for about 3 minutes before introducing the saturated solution into the capillary microreactor. Through this new approach, the heterogeneous process was transformed to the homogeneous process. With handling the experimental data at a proper operational zone, we proved that this aerobic photocatalytic oxidation of thiophenol to phenyl disulfide was second order in oxygen. The reaction rate constants could be further obtained from both the gas-liquid heterogeneous reaction and the homogeneous reaction.

With the known reaction rate constants in hand, we can calculate the Hatta number for the heterogeneous photocatalytic aerobic oxidation according to the following equation:

$$Ha = \frac{\sqrt{\frac{2}{m+1}k_{O_2,hete}(c_{O_2,in})^{m-1}(c_{sub,L})^n D_{O_2}}}{k_L} = \frac{\sqrt{\frac{2}{3}k_{O_2,hete}(C^*_{O_2})^1(c_{sub,L})^1 D_{O_2}}}{k_L}$$
(6)

where m and n are respectively the reaction orders for oxygen and thiophenol, and  $k_L$  is the liquid side mass transfer coefficient. The value of  $k_L$  is about 2.6×10<sup>-4</sup> m/s when the volumetric flow rates of 900 µl/min (gas phase) and 300 µl/min (liquid phase) are applied in the capillary microreactor.<sup>25</sup> The value of *Ha* number is then obtained (Ha = 0.06), which is obviously lower than 0.3. This low value of Ha number indicates that the photocatalytic reaction did not occur in the gasliquid interface and its very adjacent zones (cf., liquid film zone),<sup>9</sup> but it occurred in the bulk liquid phase due to the fast mass transfer rate of oxygen provided by gas-liquid Taylor flow within the capillary microreactor.

# Reaction rate constants with different photocatalyst loadings and photon flux

Experimental data show that the reaction rate constant significantly increased with increasing Eosin Y loading up to 0.5% loading. A further increase in the Eosin Y loading did not evidently increase the reaction rate constant and thus the reaction performance. In addition, the photon flux affected the reaction rate constant remarkably, especially at high photocatalyst loadings. The effect of the photocatalyst loading amount on the reaction rate constant was relatively weak at low photon fluxes. The reaction activity can be high under the excitation with high photon flux even when the photocatalyst loading is low. Therefore, the photocatalyst loading and the light source should match each other when optimizing a photocatalytic process. The following correlation based on the multiple linear regression analysis can approximately describe the relative importance of photon flux and photocatalyst loading in this gas-liquid photocatalytic oxidation (q:

 $0.29 - 1.18 \,\mu \text{mol/s}; \varphi : 0.25 - 2\%$ ).

$$k_{sub} = 228.6q^{0.56} \varphi^{0.21} \tag{7}$$

The relative deviations between the experimental and predicted values of reaction rate constants are in the range of -20 - 20% by Equation (7).

# Comparison between continuous-flow and batch processing

A glass test tube (ID: 10 mm) connected with an oxygen balloon and light source 1 were used to investigate the photocatalytic aerobic oxidation of thiophenol in batch (0.25 M thiophenol, 1 mol% Eosin Y loading and 1 equivalent TMEDA in the ethanol). In this reactor vessel, 1 or 2 mL reaction solution was agitated with a small magnetic stirrer. We found that the yield significantly increased with an increase of the stirring rate in this small batch reactor. This indicated that gas-liquid mass transfer limitations indeed occurred in batch experiments. Moreover, the yield for the 2 mL reaction mixture was lower than the one obtained in a 1 mL experiment even the same mean rate of mechanical energy dissipation ( $\varepsilon_{av}$ ) was applied. This indicates again that mass transfer limitations dominate the photocatalytic process. The obviously lower yield for 2 ml reaction mixture indicated the low mechanical energy utilization and the challenging scale-up of batch reactors, partly arising from the low mass transfer rate.

The apparent reaction rate constant of thiophenol was calculated for the 1 mL reaction mixture with the stirring rate of 1150 rpm, and its value was  $66.6 \text{ M}^{-2}\text{s}^{-1}$ . It was much lower than the intrinsic reaction rate constant (252  $\text{M}^{-2}\text{s}^{-1}$ ) obtained from the continuous-flow processing using the same light source. The mass transfer rate of oxygen from the gas phase to the liquid phase was low in the batch reactor due to its low surface-to-volume ratio. Notably, the dependence of reaction rate on the oxygen concentration is rather strong, in which the second order relation can be found according to the reaction kinetic equation. Moreover, the characteristic dimension of this small batch reactor (test tube) for photon transport was too large to get homogeneous irradiation of the reaction mixture.

#### Conclusions

We developed a compact photomicroreactor assembly that consisted of a capillary microreactor and smallscale light emitting diodes (LEDs) for the study of reaction kinetics in the gas-liquid photocatalytic oxidation of thiophenol to phenyl disulfide within Taylor flow. A suction phenomenon due to the fast consumption of oxygen was observed, indicating the importance of photons in this process. Mass transfer limitations in the photocatalytic process were evaluated and an operational zone free of mass transfer effects was chosen to study reaction kinetics. The effects of photocatalyst loading and light sources on the reaction performance were investigated. Reaction kinetic analysis was performed, and the reaction orders with respect to both thiophenol and oxygen were deduced based on heterogeneous and homogeneous experimental results, respectively.

Based on the measured reaction rate constants, the calculated Hatta number could be extremely low (i.e. Ha = 0.06). This further indicated that mass transfer limitations could be overcome by using a photomicroreactor. The reaction rate constants at different photocatalyst loadings and different photon flux were also calculated. In addition, the reaction rate constants obtained in the photomicroreactor assembly and in a batch reactor were compared, which demonstrated the advantages of this photomicroreactor assembly for the study of reaction kinetics in gas-liquid photocatalytic processes. Given the low cost prize of this photomicroreactor assembly, we anticipate that this kind of photomicroreactor assembly will find broad attraction and application in both academia and industry.

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## VARIABLE ACTIVATION ENERGIES DURING HETEROGENEOUS CATALYSIS

Trevor C. Brown<sup>1\*</sup>, David J. Miron<sup>1</sup>, Susannah L. Brown<sup>1</sup>, Abdullah K. Alanazi<sup>1</sup> and Shane M. Kendell<sup>2</sup> <sup>1</sup>University of New England, Armidale, NSW, 2351, Australia <sup>2</sup> Howard Payne University, Brownwood, TX 76801, USA

#### Abstract

The energetics of the selective oxidation of isobutane to methacrolein over phosphomolybdic acid and copper (II) phosphomolybdate catalysts have been investigated using low-pressure steady-state and temperature-programming techniques. Time-varying flexible least squares methods were used to determine variations in oxidation activation energies with increasing temperature. The solid catalysts stabilised by the third or fourth consecutive temperature-programmed run and measured activation energies increased linearly in sinusoidal waves. For catalysts, where Brønsted acidity is dominant three consecutive, single wavelength oscillations characterised activity, while for copper (II) phosphomolybdates two single wavelength oscillations were characteristic. Distinct oscillations, large amplitudes and broad ranges of activation energies indicate competing oxidation and regeneration processes as well as broad ranges of active site strengths and environments. Inclusion of copper enhances catalyst stability and reduces activity.

#### Keywords

Variable activation energies, oscillating kinetics, isobutane selective oxidation, methacrolein, phosphomolybdates.

#### Introduction

Catalytic selective oxidation of isobutane over heteropolyacids and their salts to form methacrolein and methacrylic acid is recognised as a viable and attractive alternative to current industrial methods (Sun et al., 2014; Kendell et al., 2013; Jing et al., 2014). The solid catalysts have two roles in the catalysis, an acidic role, activation of C–H bonds and a selective oxidisation role, insertion of oxygen atoms and formation of the required gas-phase products. Proton and electron transfer can occur consecutively in either order or concertedly (Efremenko and Neumann, 2012). Overall reaction for selective oxidation of isobutane to methacrolein involves three lattice oxygens [O]:

 $(CH_3)_3CH + 3[0] \rightarrow CH_2 = (CH_3)CHO + 2H_2O$ 

Detailed understanding of the processes of gas-solid reactions allows catalyst development and optimization.

A low-pressure, steady-state experimental technique has been developed to monitor the kinetics of reactions activated at solid surfaces (Sun and Brown, 2000; LeMinh and Brown, 2006; Kendell et al., 2008). Steady-state concentrations of gas-phase species evolving from a Knudsen cell reactor are monitored via mass spectrometry. Molecular flow conditions are used and cell temperature is raised at a linear rate. The challenge has been to determine accurate rate parameters from these data, and hence probe the energetics of the catalytic processes. Most commonly, rate-parameters (prefactor A and activation energy E) for gas-solid reactions are assumed to be constant and the appropriate reaction model  $f(\alpha)$ , where  $\alpha$  is reaction progress or conversion, is determined by the fit to the experimental data using the following rate law (Tan et al., 2011):

$$d\alpha/dt = A \exp(-E/RT) f(\alpha)$$
(1)

However for solid-state kinetics under non-isothermal conditions, and given surface heterogeneity, activation, deactivation, simultaneous reactions and mass transfer limitations the rate parameters are likely to vary with time and hence as temperature increases. However, the Arrhenius parameters  $A_T$  and  $E_T$  may not be specifically dependent on temperature. Due to the complexities in the kinetics, variations in the kinetic triplets ( $A_T$ ,  $E_T$  and  $f(\alpha_T)$ ) are difficult to calculate from experimental data and proposed models have been controversial (Khawam et al., 2006; Arshad and Maaroufi, 2014):

$$d\alpha_T/dt = A_T \exp\left(-E_T/RT\right) f(\alpha_T)$$
(2)

Another consideration for activation energy variations is oscillatory behaviour (Imbihl and Ertl, 1995; Rosenthal, 2011). Oscillations in heterogeneous catalytic oxidation reaction rates are observed in product concentrations and may be sinusoidal, harmonic, relaxation-type or chaotic (Kaichev et al., 2013). This behaviour is often assigned to physical changes, such as heat and mass transport effects (Imbihl and Ertl, 1995), and chemical properties such as activation and deactivation of active sites (Kokkofitis and Stoukides, 2006).

<sup>•</sup> To whom all correspondence should be addressed

Recently we have used time-varying flexible least squares methods (Kalaba and Tesfatsion, 1989) to calculate variable activation energies and prefactors for isobutane cracking over zeolites (Le Minh et al., 2012; Brown et al., 2013) and 3-methyl-2-oxetanone (βlactone) desorption from phosphomolybdates (Miron et al., 2013). Experimental data was obtained from the low-pressure, steady-state technique. In this paper flexible least squares methodology is applied to calculate variable activation energies for methacrolein formation over pure phosphomolybdic acid (H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>), pure copper (II) phosphomolybdate (Cu<sub>1.5</sub>PMo<sub>12</sub>O<sub>40</sub>) and three combined acid and copper  $Cu_{0.5}H_2PMo_{12}O_{40};$ CuHPMo<sub>12</sub>O<sub>40</sub>; salts: Cu<sub>1.25</sub>H<sub>0.5</sub>PMo<sub>12</sub>O<sub>40</sub>. Previous analyses of these data (Kendell et al., 2008, 2013) have yielded single activation energies for each catalyst.

#### Experimental

The apparatus and experimental techniques of temperature-programmed low-pressure, steady-state gas/solid reactions have previously been described (Sun and Brown, 2000; LeMinh and Brown, 2006). In summary, a molecular flow of isobutane collides, adsorbs on and reacts with the surface of ca. 0.3 g of the catalyst located in a Knudsen cell reactor. Steadystate is achieved by allowing the isobutane to flow for typically 2 hours at 100°C, before initiating a linear heating-rate of 5° C min<sup>-1</sup> to 500°C. Isobutane and product molecules eventually escape from the Knudsen cell via an exit aperture and are detected by a quadrupole mass spectrometer. Isobutane is monitored by the parent peak (m/e = 58), while products (i.e. methacrolein) are detected using characteristic peaks, m/e = 70.

Kendell et al. (2008, 2013) have previously reported the data analyzed in this paper. Mass spectral abundances for  $\beta$ -lactone, acetic acid, carbon dioxide and water, produced during oxidation over all catalysts were also monitored and recorded over the measured temperature range. For each catalyst, four consecutive and equivalent temperature-programmed runs were undertaken on each sample. Resultant mass-spectral profiles for the first two runs were inconsistent, due to large activity. As a consequence the first two temperature programmed runs for each catalyst are not reported. The 3<sup>rd</sup> run for Cu<sub>0.5</sub>H<sub>2</sub>PMo<sub>12</sub>O<sub>40</sub> and 4<sup>th</sup> run for CuHPMo<sub>12</sub>O<sub>40</sub> are particularly noisy and have also not been included.

Typical profiles for isobutane and methacrolein mass spectral abundances during temperature programming are shown in Figure 1. Here the data are from the 3<sup>rd</sup> temperature-programmed oxidation run of isobutane over phosphomolybdic acid. The raw data are denoised using wavelet methods (Percival and Walden, 2006), as indicated by the black lines in Figure 1. The R programming language (R Core Team, 2012) is used with the package "WaveThresh" to perform the signal denoising. Discrete Wavelet Transforms, within "WaveThresh" (Nason, 2013) are applied to the mass spectral abundances using the Daubechies Least Asymmetric wavelet family, with a range of vanishing moments. Weighted averages of the denoised values are then taken to determine the final wavelet denoised lines (red lines in Figure 1, and are used in all the analyses.



Figure 1. Mass spectral abundances for isobutane (filled circles) and for methacrolein (open circles) against temperature, with wavelet denoised lines (red lines are weighted average), during isobutane selective oxidation over phosphomolybdic acid (3<sup>rd</sup> run).

Rate of conversion  $(d\alpha_T/dt)$  is proportional to methacrolein abundance  $(I_{70})$ , while the reaction model,  $f(\alpha_T)$  is assumed to be a function of the isobutane abundance. And so equation (3) becomes

$$I_{70} = A_{T,\text{app}} \exp(-E_T/RT) f(I_{58})$$
(4)

with apparent prefactor

$$A_{T,\text{app}} = A_T \gamma_{70} / \gamma_{58}^{n_T} k_{\text{esc,la}}$$
<sup>(5)</sup>

and setting

$$f(I_{58}) = (I_{58})^{n_T} \tag{6}$$

Here,  $\gamma_{58}$  and  $\gamma_{70}$  are isobutane and methacrolein mass spectral sensitivity factors,  $k_{esc,Ia}$  are the isobutane escape rate constants from the Knudsen cell and  $n_T$  is an adjustable correction exponent. Substituting Equation (6) into Equation (4) and taking natural logarithms yields the following

$$\ln(I_{70}) = \ln(A_{T,app}) - E_T / RT + n_T \ln(I_{58})$$
(7)

Time-varying flexible least squares is used to determine the two rate parameters,  $E_T$  and  $\ln A_{T,app}$  and the exponents,  $n_T$  by fitting Equation (7) to the steady-state, temperature programmed data (Brown et al., 2013). The flexible least squares methodology is a

generalisation of ordinary linear regression with the inclusion of time-variant regression parameters. Time-varying flexible least squares code has been provided by Kalaba and Tesfatsion (1989) and adapted for the statistical computing language R (R Core Team, 2012). An example of fitted and apparent parameters and exponent are plotted against temperature in Figure 2 for methacrolein evolution over phosphomolybdic acid during the 3<sup>rd</sup> temperature-programmed run.



Figure 2.  $E_T$  (kJ mol<sup>-1</sup>) (red line), ln  $A_{T,app}$  (blue line) and  $n_T$  (black line) for methacrolein formation over phosphomolybdic acid (3<sup>rd</sup> Run).

#### **Results and Discussion**

The upper half of Figure 3 is a plot of activation energies against temperature for selective oxidation of isobutane to methacrolein over  $Cu_{1.25}H_{0.5}PMo_{12}O_4$ . Red dots are the 3<sup>rd</sup> temperature-programed run and blue dots the 4<sup>th</sup> run. Black dots are fitted sinusoidal curves. The following compensating prefactors are plotted in the lower half of Figure 3:

$$\log(A_{T,app}f(I_{58})) = \log(A_T\gamma_{70}/\gamma_{58}^{n_T}k_{esc,la}) + n_T \log(I_{58})$$
(8)



Figure 3.  $E_T$  (kJ mol<sup>-1</sup>) (upper) and  $log_{10} \left( A_{T,app} f(I_{58}) \right) (s^{-1})$  (lower) against temperature for methacrolein formation over  $Cu_{1.25}H_{0.5}PMo_{12}O_{40}$ ( $3^{rd}$  Run – black, and 4<sup>th</sup> Run - blue).

Variable, oscillating and increasing activation energies with increasing temperature are apparent. Fluctuations in activation energy within this hightemperature region can be effectively simulated with sinusoidal wave packets (amplitude,  $A_{osc}$  and reduced wavelength  $B_{osc}$ ), combined with linear functions (slope  $C_{osc}$  and intercept  $D_{osc}$ ):

$$E_{T,\text{osc}} = A_{\text{osc}} \sin(2\pi T/B_{\text{osc}}) + C_{\text{osc}}T + D_{\text{osc}}$$
(9)

Generalized reduced gradient methods (Kemmer and Keller, 2010) are used to optimize the four parameters in the nonlinear Equation (9) for each catalyst and temperature-programmed run. Two consecutive single wavelength sinusoidal waves are required to fit each high-temperature region data set, because in the middle of each temperature-programmed run there is a discontinuous function, either weakly increasing or jump in activation energy. Sinusoidal wave simulations are plotted with the flexible least squares data for three catalysts and two consecutive runs in Figures 4 - 6.



Figure 4. E<sub>T</sub> oscillations over H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>.



Figure 5.  $E_T$  oscillations over  $Cu_{1.25}H_{0.5}PMo_{12}O_{40}$ .

All sinusoidal reduced wavelengths ( $B_{osc}$ ) are similar with mean 44.2 ± 1.5°C. This is because experimental conditions (i.e., heating and flow rates) are equivalent for all runs and individual waves have similar temperature ranges (60 ± 4°C). The other three parameters, amplitude  $A_{osc}$ , slope  $C_{osc}$  and intercept  $D_{osc}$ are related to the catalyst and reaction energetics.



Figure 6. E<sub>T</sub> oscillations over Cu<sub>1.5</sub>PMo<sub>12</sub>O<sub>40</sub>.

Phosphomolybdate catalysts show activation energy variations with either consecutive singlewavelength oscillations for catalysts with high Brønsted acidity or three oscillations for low Brønsted acidity. Linear regression for each oscillation shows increasing activation energies for  $Cu_{0.5}H_2PMo_{12}O_{40}$  and  $H_3PMo_{12}O_{40}$  catalysts. Optimum ranges are:

$E_{T,1} = 20 - 80 \text{ kJ mol}^{-1}$	(320 – 370°C)
$E_{T,2} = 44 - 111 \text{ kJ mol}^{-1}$	(370 – 420°C)

 $E_{T,3} = 73 - 139 \text{ kJ mol}^{-1}$  (420 - 470°C)

Optimum activation energy ranges for  $CuHPMo_{12}O_{40}$ ,  $Cu_{1.25}H_{0.5}PMo_{12}O_{40}$ , and  $Cu_{1.5}PMo_{12}O_{40}$  are:

 $E_{T,1} = 36.6 - 89.1 \text{ kJ mol}^{-1}$  (320 - 370°C)  $E_{T,2} = 71 - 126 \text{ kJ mol}^{-1}$  (370 - 420°C)

Overall reproducibility of low Brønsted acidity catalyst activity, magnitudes and oscillations demonstrate highly stability, when compared with the high Brønsted acidity catalysts. The two or three discontinuous waves indicate re-oxidation of the catalyst outer-sphere during temperature programming. However, higher mean activation energies for the same temperature ranges indicate lower activity.

#### Conclusions

Time-varying flexible least squares has been used to calculate variable activation energies for methacrolein formation over phosphomolybdic acid  $(H_3PMo_{12}O_{40}),$ copper (II) phosphomolybdate (Cu<sub>1.5</sub>PMo<sub>12</sub>O<sub>40</sub>) and three combined acid and copper Cu<sub>0.5</sub>H<sub>2</sub>PMo<sub>12</sub>O<sub>40</sub>; catalysts: CuHPM012O40: Cu<sub>1.25</sub>H<sub>0.5</sub>PMo<sub>12</sub>O<sub>40</sub>. The experimental data and alternate analyses have been reported by Kendell et al. (2008, 2013). Pressure variations in both the reactant (isobutane) and product (methacrolein), evolving from the solid catalysts contained in a Knudsen cell and monitored by mass spectrometry, are included in the analyses.

Activation energies increase linearly in sinusoidal, oscillating wave packets as temperature increases for each stabilised catalyst and temperatureprogrammed run. For catalysts where the Brønsted acidity is dominant three consecutive, single wavelength oscillations characterised the activity, while for the remaining copper (II) catalysts two single wavelength oscillations were characteristic. The two or three, discontinuous waves and broad range of wave amplitudes and activation energies indicate oxidation, deactivation and activation, as well as broad ranges of active site strengths and environments.

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## RATE-REACTIVITY MODEL (RRM): A NEW BASIS FOR NON-STEADY-SATE KINETIC CHARACTERIZATION OF HETEROGENEOUS CATALYSTS

 Gregory Yablonsky<sup>\*,1</sup>, Evgeniy A. Redekop<sup>2</sup>, Denis Constales<sup>3</sup>, John T. Gleaves<sup>4</sup>, and Guy B. Marin<sup>2</sup>
 <sup>1</sup> Parks College, Saint Louis University, Saint Louis, USA
 <sup>2</sup> Laboratory for Chemical Technology, Ghent University, Technologiepark 914, B-9052 Zwijnaarde, Belgium

 <sup>3</sup> Department of Mathematical Analysis, Ghent University, Krijgslaan 281, B-9000 Gent, Belgium
 <sup>4</sup> Department of Energy, Environmental, and Chemical Engineering, Washington University in St'Louis, Brauer Hall, CB 1180, 1 Brookings Drive, Saint Louis, MO, USA 63130

#### Abstract

Precise kinetic characterization is a fundamental challenge in the field of heterogeneous catalysis, which has paramount importance for comparing the performance of different catalysts, elucidating reaction mechanisms, and constructing kinetic models. Contemporary high-throughput kinetic characterization of heterogeneous catalysts typically employs steady-state kinetic experiments which are analyzed within the standard formalism of Langmuir-Hinshelwood-Hougen-Watson (LHHW) equations. Here, a novel phenomenological form of kinetic models is presented for systematic evaluation of non-steady-state kate. The observable quantities within this Rate-Reactivity Model (RRM) are the time-dependent concentrations C(t), net production rates R(t), and integral surface uptakes U(t) of different gas species. The model is linear with respect to the observable quantities and their pairwise combinations. The coefficients of the model, i.e. phenomenological reactivities, uniquely characterize a given catalyst state and can be thought of as generalizations of sticking coefficients.

#### Keywords

Rate-Reactivity Model (RRM), non-steady-state kinetics, phenomenological model, Temporal Analysis of Products (TAP)

#### Introduction

Kinetic characterization of catalytic reactions is an integral part of fundamental research in catalysis, development of new catalytic materials, and optimization of industrial catalytic processes (Marin and Yablonsky, 2011). The amount of information extracted from kinetic data and its reliability strongly depend on the experimental methodology, but the form in which kinetic models are formulated to evaluate these kinetic data is also very important. Steady-state kinetic experiments widely employed in contemporary catalysis research are typically interpreted within the framework of global Turnover Frequencies (TOF) or, at best, Langmuir-Hinshelwood-Hougen-Watson (LHHW) equations. Although LHHW models can in principle be derived from the detailed microkinetics, these equations are essentially phenomenological, meaning that they are readily used to process kinetic data without prior microkinetic justification. For the non-steady-state kinetic experiments, such convenient and standardized phenomenological framework is still missing, which impedes a widespread application of

this rich source of mechanistic information for systematic qualitative studies in catalysis.

The **Rate-Reactivity** Model (RRM) introduced herein aims at fulfilling this gap in the methodological toolkit of catalytic kinetics. For all measurable gas species involved in a catalytic reaction, the RRM equations linearly relate the transformation rates, concentrations, and integral surface uptakes as well as pairwise combinations of all these timedependent quantities. The coefficients of the linear model, i.e. reactivities, uniquely characterize a given catalyst state which must be well-defined and relatively constant during the kinetic measurement. The model is based on the Temporal Analysis of Products (TAP), an experimental technique employing small perturbations (pulses) to measure the kinetics exhibited by welldefined and spatially uniform catalyst states (Gleaves et al., 2010). The time resolution of a single TAP pulse-response experiment is on the order of milliseconds. Moreover, long sequences of such pulses and alternating pulses with controlled time delay offer a diverse menu of experiments for studying a variety of catalytic phenomena occurring across several time scales. Empirical reactivities, coefficients of the RRM equations, can be used either as standard kinetic descriptors to characterize different catalytic materials or as the basis for more in depth interrogation of the reaction mechanisms and for microkinetic modeling.

#### Experimental basis and primary data

The prerequisite to the development and application of the RRM is a set of time-dependent transformation rates and species concentrations which are measured in such a way as to minimize the alterations of the catalyst state. Temporal Analysis of Products (TAP) is an advanced non-steady-state technique which satisfies these requirements and provides high-fidelity rate/concentration transients with millisecond time resolution. The details of TAP methodology can be found in multiple reviews (Gleaves et al., 2010, Pérez-Ramírez and Kondratenko, 2007). In brief, during a typical TAP experiment a small (10<sup>-9</sup> mol) and narrow (100 µs) pulse of gas is admitted into an evacuated (background pressure of 10-<sup>4</sup> Pa) microreactor containing a catalytic sample. The gas molecules under these conditions traverse the packing solely via Knudsen diffusion which provides a well-defined standard transport process. Unreacted ot newly produced gas molecules eventually egress from the reactor outlet into an adjacent vacuum chamber, where they are continuously monitored by a calibrated Quadrupole Mass Spectrometer (QMS). Each pulse typically contains orders of magnitude less molecules than the number of active sites on the catalyst and, thus, can be considered as a "state-defining" small perturbation.

The thickness of the catalytic bed inside the microreactor is typically kept significantly smaller than the total reactor length, the rest of the space being packed with inert particles, in order to minimize the macroscopic non-uniformity within the sample (Shekhtman et al., 1999). The rates and gas concentrations inside the uniform catalytic bed can be obtained from the recorded exit flow-rates with no kinetic assumptions (model free) via an algorithm based on the solution of inverse diffusion problem in the Fourier domain, the so-called Y-Procedure (Yablonsky et al., 2007). The resulting rates can be further processed to yield the time-resolved integral uptakes of various gas substances on the catalyst surface (U) (Redekop et al., 2011):

$$U_X(t) = \int_0^t R_X^+(\tau) d\tau - \int_0^t R_X^-(\tau) d\tau, \quad (1)$$

Together with the rates and concentrations, the integral uptakes constitute the primary data set for the application of RRM, i.e. R(t), C(t), U(t).

#### **Rate Reactivity Model (RRM)**

The rate of chemical transformation of a gas substance in contact with a solid material is a complex function of the gas phase composition, composition and structure of the solid, temperature, and other process conditions. To relate rates to some intrinsic properties of a solid material, it is useful to represent non-steady-state kinetic data by the following equation (2)

$$R_{l}(t) = \sum_{k=1}^{N} \psi_{l,k}^{C} C_{k}(t) + \sum_{j=1}^{M} \psi_{l,j}^{U} U_{j}(t) + \sum_{k=1}^{N} \sum_{j=1}^{M} \psi_{l,k,j}^{CU} C_{k}(t) U_{j}(t) + \sum_{l=1}^{M} \sum_{j=1}^{M} \psi_{l,l,j}^{UU} U_{l}(t) U_{j}(t) + \psi_{l,0}$$

where N is a number of gas species involved in reaction and M is a number of independent mass balances between the gas and surface phases. The transformation rate of *i*th gas species on the left hand side of this equation is defined in a conventional manner as for products and for reactants.

The first term on the right hand side is the sum of reaction rates corresponding to the steps in which gas i is produced or consumed as a result of direct gas-solid interactions between the active solid and each individual gas present in the reaction environment. Each term in this sum is characterized by certain reactivity  $\Psi^{C}_{i,k}$  which has the dimensions of an apparent rate constant, 1/s, and reflects the ability of the solid material to transform the gas phase composition. The RRM Equation is linear with respect to the gas phase concentrations  $C_i$  following a common, and usually strongly justified, assumption that only one gas molecule participate in an elementary gas-solid reaction. The second term is the sum of reaction rates of those processes in which gas i is produced by the surface without the direct participation of any gases and which rates are proportional to the integral gas uptakes. The corresponding reactivities  $\Psi^{U}$ *ii* have the dimension of a desorption rate constant.

**The following two terms** of the RRM equation (2) are the sums of reaction rates of those processes in which gas substance *i* is produced or consumed via process which rates are proportional to both, gas concentrations and integral uptakes or to more than one uptake at the same time. **The last term** on the right hand side, the 'zero' reactivity  $\psi_{i,0}$  represents the ability of the solid to produce a gaseous product *i* without direct participation of other gases or species contributing to surface uptakes. These terms have the dimensions of a reaction rate.

In special cases when the uptakes are strongly correlated with specific surface intermediates and the experiment is closely approaching the state-defining limit, the RRM model drastically simplifies. For example, only the first term ( $\psi^{C}C$ ) will contribute to the rate of a completely irreversible reaction in a statedefining experiment, i.e.  $R_r(t) = R_p(t) = k_{app}C_r(t)$ . Here, the reactant's reactivity with respect to itself and the products reactivity with respect to the reactant are equivalent to the apparent rate coefficient. From the gas-phase prospective, the entire process can be represented as an instantaneous transformation of impinging reactants into adspecies or further into products, if the surface steps and desorption of products are fast. The same is true for a reversible reaction with very fast desorption steps, i.e. the rates  $R_r(t) = R_p(t) = k^+ C_r(t) - k^- C_p(t)$ . In this case,

each gas has a pair of two non-zero reactivities which

are equivalent to the forward and reverse apparent rate coefficients. If the desorption steps are not much faster than the rest but the experiment is still state-defining, the second term  $(\psi^U U)$  will also contribute to the overall rate. For example, for a simple reversible adsorption of gas *i* in the limit of small coverage:  $R_i(t) = k^+ C_i(t) - k^- U_i(t)$ . The analysis of Further complications of the reaction kinetics might justify introduction of the cross-terms ( $\psi^{CU}CU$  or  $\psi^{UU}UU$ ), but such model extensions can be performed in a judicial manner up to, but not exceeding, an optimal model complexity.

Methodologically, the main distinguishing feature of the RRM model is that the focus is temporarily shifted from detailed mechanism to phenomenological of characterization. Instead attempting to describe the reaction as a network of elementary steps involving hypothetical surface intermediates, the observed rates are expanded as linear combinations of experimentally observable concentrations and uptakes. In simplest cases, the RRM representation might coincide with the corresponding microkinetic model, especially when the integral uptakes are equivalent to the concentrations of specific surface intermediates or at least to their linear combinations. In general, however, the concentrations of surface intermediates cannot be represented by linear combinations of uptakes. Nevertheless, the RRM representation in these cases can still be robust. The reactivities derrived from the RRM as empirical quantities can be readily used for comparative catalyst characterization, but they also have certain physicochemical meaning. On the next level of analysis, this information can be used to formulate sound mechanistic hypotheses which can then be tested via conventional regression of the original data.

Another important point about the RRM equation should be stressed: only those surface species that change considerably within a single measurement contribute to the dynamic surface uptakes (U) entering the RRM equation. Concentrations of those surface species which remain largely unperturbed by a small perturbation during a single measurement enter the equation through various reactivities  $\psi$ , quantities which generally depend on the catalyst state. Since instantaneous reactivities are determined by the catalyst state via a priori unknown relations, they may be history-dependent. But they are not functions of the instantaneous gas composition.

The RRM representation of non-steady-state kinetics comply with the general approach of Interrogative Kinetics (Gleaves et al., 1997, Shekhtman et al., 2003), according to which small perturbations are used to take "kinetic snapshots" of a series of welldefined catalyst states. Some of the mechanistic fingerprints are revealed by the gas responses within a single "snapshot", while others are revealed by the evolution of "snapshots" over a range of catalyst states spanning a scale, e.g. between reduced and oxidized states or clean surface and coked surface. Depending on their stability between the pulses, individual catalyst states can be prepared for taking the "snapshot" in a series of many equispaced pulses (for stable states) or in a pump-probe experiment with precisely controlled time-delay (for unstable states). Therefore, the RRM reactivities can be used as robust kinetic descriptors of catalytic activity exhibited by specific catalyst states, much like sticking coefficients are used as kinetic descriptors of adsorption activity in surface science.

It should be pointed out that the RRM generalizes previously published results which employed similar concepts for kinetic data analysis, For example, the model-free albeit implicitly. rate/concentration data obtained from TAP via the Y-Procedure were analyzed in terms of linear relations to obtain empirical rate coefficients (reactivities) for irreversible oxygen adsorption on polycrystalline Pt (Redekop et al., 2011) and reversible CO adsorption on supported Pt catalyst (Redekop et al., 2013). Furthermore, several competing pathways of CO oxidation were theoretically analyzed using linear relations between the rates, concentrations, and uptakes (Redekop et al., 2014). Earlier, Shekhtman et al., 2003 developed a phenomenological model in which the rates are also linearly related, but to the concentration time-derivatives of different order by the "primary kinetic coefficients" or Laplace reactivities. Their model, also based on TAP, was successfully applied in several experimental studies (e.g. Shekhtman et al., 2008), and can be considered as a formulation of transient kinetics complementary to the RRM. Other transient techniques (e.g. Shannon and Goodwin, 1995, Visselli et al., 2011) can broaden the application of the RRM in the future, if they will eventually provide the quantitative set of rate/concentration transients for well-defined catalyst states.

#### **Conclusions and perspectives**

The phenomenological Rate-Reactivity Model was suggested as a basis for systematic non-steadystate kinetic characterization of heterogeneous catalysts. The primary data set for the RRM contains time-dependent transformation rates (R), gas concentrations (C), and integral uptakes (U) which are available, for example, from the Thin-Zone TAP experiments. The RRM equation linearly relates these R(t)-C(t)-U(t)transients their and pair-wise combinations to each other using empirical coefficients, reactivities, which uniquely characterize the ability of catalytic material in a well-defined state to alter the composition of the gas phase.

The main advantage of using the RRM equation to interpret kinetic data is that the ability of a specific catalyst state with known history to alter the gas composition is conceptualized and measured as an empirical quantity, i.e a number or a set of numbers. In our opinion, it is methodologically valuable to infer such quantities from experimental kinetic data and to understand their physico-chemical meaning before resorting to model fitting. Contrary to combinatorial fitting of microkinetic models, the RRM equation reflects only general physico-chemical knowledge about gas-solid reactions and does not involve specific mechanistic assumptions, which are more difficult to justify and should not be accepted prematurely.

In our future works, we will combine the RRM approach with the recently introduced concepts of kinetic coherency and momentary equilibrium to develop a more powerful, robust strategy for precise non-steady-state kinetic characterization of complex heterogeneous catalysts and other functional materials.

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## A HETEROGENEOUS MULTI-SCALE DYNAMIC MODEL FOR SIMULATION OF CATALYTIC REFORMING REACTORS

Grigorios Pantoleontos<sup>\*</sup>, George Skevis, George Karagiannakis, Athanasios G. Konstandopoulos Aerosol & Particle Technology Laboratory, Chemical Process & Energy Resources Institute, Centre for Research & Technology Hellas, 6<sup>th</sup> km Charilaou-Thermi Road, P.O. Box 60361, 57001, Thessaloniki, Greece pantole@cperi.certh.gr; gskevis@cperi.certh.gr; gkarag@cperi.certh.gr; agk@cperi.certh.gr

#### Abstract

The present work aims to evaluate the performance of catalytic reforming systems by developing a generic 1-D dynamic model coupled with heterogeneous reaction schemes in catalytic reactors. The novelty of the numerical model stems from the direct inclusion of inter-particle (fluid-to-particle), intra-particle (within particle) and intrabed heat and mass transport resistances under transient conditions. The developed model accounts for multi-component gas mixture physico-chemical properties and correlations for calculating mass and heat transfer coefficients. Effective macroscopic properties within the particle can be calculated by incorporating diffusivities and conductivities of the porous network characteristics accounting for Knudsen and molecular transport, as well as tortuosity and porosity of the overall porous path. The industrial case of a steam-methane reforming (SMR) multi-tubular reactor was studied as the most representative case, with all mass/energy resistances present under severe pressure and temperature conditions. It was shown that there are severe diffusional limitations within the particle, while there are also temperature and partial pressure gradients due to the heat and mass transport resistances in the particle film layer. The proposed formulation is capable of reproducing published data with reasonable accuracy, while the results are in accordance with relevant literature findings.

#### Keywords

Steam methane reforming, catalytic reactors, dynamic simulation.

#### Introduction

The oxidative method of hydrocarbons reforming is given by the general reaction scheme:  $C_nH_m + [Ox] \longleftrightarrow xH_2 + yCO + zCO_2$ 

where [Ox] is the oxidant. The process is exothermic if  $[Ox]=O_2$ ; endothermic if  $[Ox]=H_2O$ ,  $CO_2$ ,  $H_2O-CO_2$  mixtures; thermal neutral if [Ox]=mixtures of  $O_2$ -H<sub>2</sub>O,  $O_2$ -CO<sub>2</sub>, or  $O_2$ -H<sub>2</sub>O-CO<sub>2</sub> in appropriate stoichiometric quantities. Since steam,  $CO_2$  and  $CH_4$  are rather inert, catalysts are widely used to accomplish these processes at the practical range of temperatures (750-950°C).

Including  $CO_2$  in the reforming reaction scheme is called dry reforming of methane (DRM). DRM takes place at ~800-1000°C temperature and 1-20 bar pressure and produces syngas (CO + H<sub>2</sub>) via the reaction:

 $CH_4 + CO_2 \longleftrightarrow 2CO + 2H_2 (-\Delta H_{298} = -247 \text{ kJ/mol}) (R1)$ 

Syngas can be used as feedstock for the production of added value chemicals such as methanol, dimethyl-ether (DME), olefins, etc. or for the production of refinery products via the Fischer-Tropsch synthesis route such as sulfur-free diesel, naptha, LPG, etc. Alternatively, syngas can also be used by separating and supplying hydrogen as an energy carrier, supporting a hydrogen based economy. Currently, the main industrial path for the production of syngas involves natural gas  $(CH_4)$  via the steam methane reforming (SMR) reaction scheme (Carrara et al., 2010):

$$\begin{array}{l} CH_4 + H_2O \longleftrightarrow CO + 3H_2 \ (-\Delta H_{298} = -206 \ kJ/mol) \ (R2) \\ CO + H_2O \longleftrightarrow CO_2 + H_2 \ (-\Delta H_{298} = 41.2 \ kJ/mol) \ R3) \\ CH_4 + 2H_2O \longleftrightarrow CO_2 + 4H_2 \ (-\Delta H_{298} = -165 \ kJ/mol) \ (R4) \end{array}$$

where (R3) is the water gas-shift reaction (WGS).

Following Hill's (1977) method, since 3 or more reactions are written for a given system, it is mandatory to determine whether there is a linear combination of two or more. To test for independence, it is convenient to form the stoichiometric coefficients matrix, and by rearranging using Gauss elimination method to eventually have:

-1	-1	2	2	0		1	1	-2	-2	0
-1	0	1	3	-1	_	0	1	-1	1	-1
0	1	-1	1	-1	-/	0	0	0	0	0
-1	1	0	4	-2		0	0	0	0	0

This proves that only 2 out of 4 reactions are linearly independent and thus only 2 reaction extents are necessary in order to define the equilibrium

<sup>•</sup> To whom all correspondence should be addressed

expressions of the reaction scheme. The two extents (equally, conversions,  $x_{CH4}$ ,  $x_{CO2}$ ) of the reaction scheme can be conveniently taken from Eq. (R2 & R3) to account for CH<sub>4</sub> and CO<sub>2</sub> conversions, where in each reaction only CH<sub>4</sub> and CO<sub>2</sub> are present, respectively.

When a chemical reaction occurs within a porous network, its behaviour may appreciably deviate from 'true' chemical kinetics: that is the intrinsic reaction rate (Weisz & Hicks, 1962). Concentration/temperature profiles in porous media are developed when diffusion and reaction occur simultaneously. When diffusional transport is very fast c.f. reaction rate, the whole internal area of the catalyst is readily functional for the reaction (Karanth & Hughes, 1974): the observable kinetic rate is the same as the intrinsic. Otherwise, it is anticipated that reactants do not have the time to diffuse in/from the active part of the catalyst; this is the usual case in industrial catalytic applications. In the latter case catalyst activity is reduced and in order to account for this phenomenon the catalyst effectiveness factor  $(\eta)$  is used.

The observable/apparent reaction rate,  $Rate_{avg}$ , is derived by the following equation:

$$Rate_{avg} = j \int_0^1 Rate_{intr} \times \xi^{j-1} d\xi$$
<sup>(1)</sup>

with j=1, 2, 3 for slab, cylindrical or spherical geometry, respectively; where  $\xi$  (=r/R<sub>p</sub>) is the dimensionless radial distance ranging in [0, 1].

Eventually the effectiveness factor for reaction i is defined as (Pantoleontos et al., 2012):

$$n_{\rm i} = \frac{j \int_0^1 r_{\rm intr} \left( p_s \right) \cdot \xi^{j-1} \,\mathrm{d}\,\xi}{r_{\rm intr} \left( p \right)} \tag{2}$$

#### Model formulation

In the present work, the following assumptions are made in order to describe the fluid flow within the reactor and the transport of the gaseous components through the porous network (Pantoleontos et al., 2012): a) no radial gradients in the bed; this is a valid assumption as long as the reaction scheme is not exothermic. The heat provided at the reactor's walls is simulated by an overall heat transfer coefficient, U, that depends only on the axial direction of the reactor; b) pseudo-continuous heterogeneous model; these models rely on the assumption that significant changes in the dependent variables take place at a scale larger than the size of the catalyst particle; c) all particles are of the same size and the voids between are evenly distributed; e) no side or homogeneous reaction occurs. Considering these assumptions mass and energy balances in a catalytic container have the following formulation:

$$\frac{\varepsilon_{\rm B}}{u_{\rm s}}\frac{\partial x_{\rm CH_4}}{\partial t} + \frac{\partial x_{\rm CH_4}}{\partial z} - \frac{\varepsilon_{\rm B} \cdot D_{\rm ax}}{u_{\rm s}}\frac{\partial^2 x_{\rm CH_4}}{\partial z^2} = \frac{\Omega \cdot \rho_{\rm B}}{F_{\rm CH_4,o}} \left(\eta_{\rm CH_4} r_{\rm CH_4}\right)$$
(3)

$$\frac{\varepsilon_{\rm B}}{u_{\rm s}} \frac{\partial x_{\rm CO_2}}{\partial t} + \frac{\partial x_{\rm CO_2}}{\partial z} - \frac{\varepsilon_{\rm B} \cdot D_{\rm ax}}{u_{\rm s}} \frac{\partial^2 x_{\rm CO_2}}{\partial z^2} = \frac{\Omega \cdot \rho_{\rm B}}{F_{\rm CH_4,0}} \left( \eta_{\rm CO_2} r_{\rm CO_2} \right)$$
(4)

$$\rho_{g} \cdot c_{p} \cdot \varepsilon_{B} Le \frac{\partial T}{\partial t} + \rho_{g} c_{p} u_{s} \frac{\partial T}{\partial z} - \varepsilon_{B} \cdot \lambda_{ax} \frac{\partial^{2} T}{\partial z^{2}} =$$

$$\rho_{B} \sum_{i=1}^{3} \eta_{i} r_{i} \left(-\Delta H_{i}\right) - 4 \frac{U}{d_{i}} \left(T - T_{w}\right)$$

$$- \frac{dp}{dz} = \frac{f \rho_{g} u_{s}^{2}}{2R_{p}}$$
(5)
(6)

where 
$$\frac{F_{j,o}}{\Omega} = C_{j,o} \times u_s$$
, for j=CH<sub>4</sub>, H<sub>2</sub>O, CO, H<sub>2</sub>, CO<sub>2</sub>

and Le is the Lewis number defined in Jensen & Ray (1982). The other parameters/variables are:

u<sub>s</sub>: superficial velocity;  $\varepsilon_B$ : bed porosity; D<sub>ax</sub>: effective axial diffusivity; r<sub>i</sub>: reaction rate of *i* reaction; F<sub>j,o</sub>: initial flowrate of *j* component;  $\Omega$ : cross sectional area of the catalytic container; C<sub>j</sub>,o: initial concentration of *j* component;  $\rho_B$ : bed density;  $\rho_g$ : gas density; c<sub>p</sub>, c<sub>p,s</sub>: heat capacities of gas mixture and catalyst, respectively; T, T<sub>w</sub>: gas mixture and wall temperatures, respectively; d<sub>i</sub>: inner diameter of the container tube; p: total pressure; f: friction factor; R<sub>p</sub>: catalyst radius.

Applying Danckwerts boundary conditions (BCs) leads to (Danckwerts, 1953):

$$u_{s}x_{j,o} = u_{s}x_{j} - \varepsilon_{B}D_{ax}\frac{\partial x_{j}}{\partial z}\Big|_{z=0}$$
 for j=CH<sub>4</sub>, CO<sub>2</sub> (7)

$$\frac{\partial x_j}{\partial z}\Big|_{z=L} = 0 \text{ for } j = CH_4, CO_2$$
(8)

$$\rho_{g}c_{p}u_{s}T_{0} = \rho_{g}c_{p}u_{s}T - \varepsilon_{B}\lambda_{ax}\frac{\partial T}{\partial z}\Big|_{z=0}$$
(9)

$$\frac{\partial \mathbf{T}}{\partial z}\Big|_{z=L} = 0 \tag{10}$$

where  $x_{j,o}$  is the initial conversion for component j. Note that,  $x_{j,o}=0 \forall j$ .

For total pressure in the packed-bed:

$$p=p_0, \text{ at } z=0 \tag{11}$$

Initial conditions (ICs) are defined as:  $x_j(0,z)=0$  for  $j=CH_4$ ,  $CO_2$  (12)  $T(0,z)=T_0$  (13)

The mass continuity equations in the particle have to be integrated in order to obtain the partial pressure profiles (considering spherical particles) for  $j=CH_4$ , CO<sub>2</sub>:

$$-\mathbf{D}_{\rm eff,j} \frac{1}{\xi^2} \frac{\partial}{\partial \xi} \left( \xi^2 \frac{\partial \mathbf{p}_{\rm s,j}}{\partial \xi} \right) = \mathbf{R} \mathbf{T} \mathbf{R}_{\rm p}^2 \boldsymbol{\rho}_{\rm s} \mathbf{r}_{\rm j}$$
(14)

The dependent variables,  $p_{s,j}$ , are the partial pressure of the gaseous components in the particle;  $D_{eff}$  is the effective diffusivities within the particle accounting for Knudsen diffusion and the effective properties of the catalytic particle.

Introducing  $T_s$  (temperature in the particle) the particle energy equation is defined as (Ghouse & Adams, 2013):

$$R_{p}^{2}\left[\left(1-\varepsilon_{c}\right)\rho_{c}c_{p,s}+\varepsilon_{c}\sum_{i=1}^{N}c_{p(molar),i}\frac{\mathbf{p}_{s,i}}{RT_{s}}\right]\frac{\partial T_{s}}{\partial t}$$

$$-\lambda_{cat}\frac{1}{\xi^{2}}\frac{\partial}{\partial\xi}\left(\xi^{2}\frac{\partial T_{s}}{\partial\xi}\right)=R_{p}^{2}\rho_{c}\sum_{i=1}^{n}\mathbf{r}_{i}\left(-\Delta\mathbf{H}_{i}\right)$$
(15)

BCs for the particle Eqs. can be defined as:

$$\frac{\partial \mathbf{p}_{s,j}}{\partial \xi}\Big|_{\xi=0} = 0 \tag{16}$$

$$D_{eff} \left. \frac{\partial \mathbf{p}_{s,j}}{\partial \xi} \right|_{\xi=1} = R_p k_{film} \left( \mathbf{p}_j - \mathbf{p}_{s,j} \right|_{\xi=1} \right) \tag{17}$$

$$\frac{\partial T_s}{\partial \xi}\Big|_{\xi=0} = 0 \tag{18}$$

$$\lambda_{eff} \frac{\partial \mathbf{T}_{s}}{\partial \xi} \Big|_{\xi=1} = R_{p} h_{film} \left( T - T_{s} \Big|_{\xi=1} \right)$$
(19)

Particle BCs (16) are of Robin type (mixed Neumann and Dirichlet), actually coupling the set of equations for the bed and the particles by correlating the partial pressures and temperature in the particle with those in the bed. In this respect, it is expected that there is a finite gradient at the surface of the particle, which is imposed by the presence of the film layer resistance. That is, mass flux -in terms of partial pressures- (given by the term  $D_{eff} \frac{\partial p_{s,j}}{R_n \partial \xi} \Big|_{\xi=1}$ ) and

energy flux (given by the term  $\lambda_{eff} \frac{\partial T_s}{R_n \partial \xi} \Big|_{\xi=1}$ ) at the

surface of the particle are correlated with a linear driving force: the difference of partial pressures and the difference of the temperatures from the bulk phase to the surface of the particle, respectively. Thus, the gaseous components have to overcome this extra resistance to transport.

In this work, the IC for Eq. (15) is set to  $T_0$ ; the particle mass balance equation [Eq. (14)] IC is set by solving this equation without the reaction terms; this allows the numerical solver to determine consistent initialization by providing equations of physical meaning at the beginning of the simulation at particle level.

The above coupled bed-particle equations was solved in the equation-based software gPROMS 4.0. Physico-chemical properties and correlations are calculated according to the methodology presented in Pantoleontos et al. (2012).

#### **Results and discussion**

In order to validate the model, it is convenient to compare with results derived from the modeling and simulation of an established case. A major cause of results discrepancies amongst literature findings lies on the vast application of different correlations. Especially where heat integration is concerned, there is a large number of overall wall-bed heat transfer coefficient

which ultimately determine correlations heat facilitation and in turn the degree of conversion. The industrial case of steam methane reformer (SMR) is an excellent candidate for model validation and evaluation because of the significant number of literature articles devoted on this subject.

Table 1 presents data for the simulation of an industrial SMR; reaction rates are calculated based on the formulas presented by Xu & Froment (1989). The ultimate target of this simulation is to be close to the value by Plehiers & Froment (1989) for the dry molar fraction of  $H_2$  to be equal to 0.645-0.654. The wall heat provided to the reactor is matched by a quadratic wall temperature profile with respect to axial coordinate (Pantoleontos et al., 2012):  $T_w = 1000.4 + 12.145 z +$  $0.011 \text{ z}^2$ .

Table .	1:	Data	for	the	SMR	process.
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Parameter	Value
To	793.15 K
L	12 m
$\rho_s$	2355.2 kg/m <sup>3</sup>
τ	3.54
d <sub>p,e</sub>	0.0173 m
$d_{p,i}$	0.0084 m
$d_{tube,i}$	0.1016 m
d <sub>tube,o</sub>	0.1322 m
F <sub>CH4,o</sub>	5.17 kmol/hr
F <sub>H2O,o</sub>	17.35 kmol/hr
F <sub>H2,o</sub>	0.63 kmol/hr
F <sub>CO2,0</sub>	0.29 kmol/hr
F <sub>N2,0</sub>	0.85 kmol/hr
po	25.7 bar
$\lambda_{\rm s}$	0.3489 W/(m K)



Figure 1. Wall heat and temperatures under steadystate operation

As seen in *Figure 1* the wall temperature,  $T_w$ , must be adequately high in the reactor's inlet area to facilitate the endothermic reaction scheme.  $T_w$ increases along the z-axis with the gas mixture temperature, T, but their difference is gradually decreased, which entails that lower heat input is required closer to the exit of the reactor. Integration of the area under wall heat curve (and dividing by the

reactor's length) provides the overall heat duty of the reforming process, which is 80 kW/m<sup>2</sup>, well within the range of a typical industrial SMR requiring total wall heat input in the range of 45-90 kW/m<sup>2</sup> (Rostrup-Nielsen, 1984).

As illustrated in *Figure 2*,  $H_2$  is produced at the expense of steam and CH<sub>4</sub> with a total pressure decrease from 25.7 to 23.33 bar. At the exit, the dry composition is 66.2% very close to that calculated by Plehiers & Froment (1989). As temperature increases, the reverse WGS (reverse R3) is enhanced threby leading to CO formation at the expense of CO<sub>2</sub> and H<sub>2</sub>.



Figure 2. Molar fractions and total pressure under steady-state operation.

Figure 3 depicts the dynamic profiles of the temperature difference of the catalyst core and the gas bulk phase at various axial points. It is evident that the catalyst does not reach the gas mixture temperature rapidly due to the solid catalyst thermal inertia. This difference may be lower than -50 K at the exit of the reactor for short times, but it becomes very small under steady-state conditions reached after about 120 s for all points along the z-axis. However, this difference is never eliminated, due to the mass and heat inter- and intra-particle resistances.



Figure 3. Dynamic profiles of temperature difference between the catalyst core and the gas mixture at various z-points.

#### Conclusions

The current work reports a generic 1-D model of heterogeneous reaction schemes in catalytic containers. All resistances to mass and heat transfer in the bed, the bed-to-particle region (inter-particle), and the particle (intra-particle) itself are included under transient conditions.

In order to validate the developed model, the industrial case of the SMR reactor was set as a basecase; this is done because all resistances are present in severe pressure and temperature conditions for the multi-component feed gas mixture. It is shown that there are indeed significant diffusional limitations within the particle, while there are also temperature and partial pressure gradients due to the heat and mass transport resistances in the particle film layer. The proposed formulation is capable of reproducing published data with reasonable accuracy, while results are in accordance with literature findings.

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# EFFICIENT METHOD FOR THE CALCULATION OF RATE COEFFICIENTS OF ELEMENTARY REACTIONS IN THE GAS PHASE

A. Koksharov<sup>\*</sup>, M. Pfeifle, V. Bykov, U. Maas, M. Olzmann Karlsruhe Institute of Technology (KIT) Karlsruhe, Germany

Keywords

Reaction Rates, Master Equation, Numerical Solution, Spectral Method, Pressure Dependence, Unimolecular Reactions

The dependence of rate coefficients on system parameters such as pressure and temperature is often complicated, especially when unimolecular steps are involved. One of the possible ways to describe this dependence quantitatively involves the solution of a master equation (ME). The ME describes the time-dependent evolution of the distribution of a reactant/intermediate with respect to its vibrational and rotational energy levels under the influence of chemical reactions and collisional energy transfer to/from the surrounding bath gas.

The ME can be solved analytically only in a few special cases. In most practical applications, a numerical solution is necessary. This is normally achieved by a discretization of the continuum form of the ME in the internal energy domain. Besides an upper energy cut-off, often a rather small energy increment is required in the discretization to achieve reasonable accuracy. This leads to a large linear system with up to several thousands of variables, especially when reaction systems with multiple coupled chemical species (multi-well reactions) are considered. Therefore, the calculation of rate coefficients for many pressures and temperatures can become quite computationally demanding.

In this contribution, a quasi-spectral method is suggested, which permits to solve the ME with a small number of variables (less than a hundred) without a significant loss of accuracy. The corresponding speed-up compared to the conventional method is of several orders of magnitude, if system set-up costs are not considered. The resulting linear system is expressed in terms of weights of irregularly distributed Gaussian radial basis functions (GRBF). The method is based on the projection of the continuous ME onto the space of GRBFs. The results of our newly proposed method are compared with those of the conventional method. As a case study for systems of coupled unimolecular reactions, we have chosen the mutual isomerization of the  $C_3H_4$  species propyne and allene. Using this example, the novel approach is validated over a large temperature and pressure range and its performance is demonstrated.

# New Observation of Water Gas Shift Equilibrium in Flames

Wendong Wu, Gregory Yablonsky, Richard L Axelbaum Washington University in St. Louis St. Louis, MO 63130

Keywords

Water-gas-shift, partial-equilibrium, diffusion flame, equilibrium domain, cyclic reactants

The kinetic behavior of the water-gas-shift (WGS) sub-system was studied computationally for hydrocarbon flames in the counter-flow geometry. Special attention was paid to the domain in which the reactions in the WGS-complex exhibit characteristics that lead to species concentrations approaching those expected from equilibrium. Two scenarios were observed for WGS equilibrium:

(1)'detailed' equilibrium in which every step of the WGS-mechanism is nearly in equilibrium;

(2)apparent 'counter equilibrium' which is achieved via opposing but coherent shifts away from equilibrium for two reactions. This interesting phenomenon is caused by the supply of H radical to the system. The hydrogen radical is a 'counter' reactant, i.e. a reactant of the first reaction, and a product of the second reaction.

Parametric domains where found in which these two scenarios are observed. For a given fuel type, it was shown that the two scenarios can be separated by the location of stoichiometry. On the oxidizer side, the detailed equilibrium of overall WGS reaction is achieved while on the fuel side, the apparent 'counter' equilibrium can occur.
Poster abstracts

# KINETICS OF O3 UPTAKE ONTO INDOOR SURFACES AND SECONDARY VOC EMISSIONS IN A CLASSROOM

Michael K. M. Ward<sup>\*</sup>, Maxence Mendez, Sylvie Gosselin, Nicolas Visez and Coralie Schoemaecker CNRS-Université Lille 1 – Labo PC2A Villeneuve d'Ascq, F-59655

Keywords

Ozone uptake, Indoor air quality, volatile organic compounds.

Ozone,  $O_3$ , is an important pollutant in both the indoor and outdoor environments. In particular, ozone can act as an oxidant in the gas-phase *via* the ozonolysis of unsaturated Volatile Organic Compounds (VOCs) [1]. Furthermore,  $O_3$  can react heterogeneously with surface-adsorbed unsaturated non-VOC species, such as those found in human skin oils and sebum (*e.g.* squalene), initiating secondary emissions of product VOCs into the gas-phase [2]. Thus, reactions of ozone at the air-surface interface can potentially alter the VOC budget of indoor environments and the processes of such chemistry must be identified and characterized.

In addition to the aims of the MERMAID project [3], the reactivity of  $O_3$  with a number of surfaces within a low energy building secondary school classroom has been investigated using a Field and Lab Emission Cell (FLEC).  $O_3$  levels were measured using a commercial UV detector and VOCs *via* a time-of-flight proton-transfer-reaction mass-spectrometer. Offline measurements of VOC were made by HPLC-MS and non-VOC species from the studied surfaces by GC-MS. The emission of a number of oxygenated VOC species has been observed and the temporal profiles of these species, as well as  $O_3$ , have been used in optimising a model describing the uptake of  $O_3$  on each surface investigated and the ozonolysis reaction of unsaturated organic surface species.

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## STABILITY OF IPRODIONE IN AOT-BASED REVERSE MICELLES UNDER ALKALINE CONDITIONS

J. Morales<sup>a,\*</sup>, A Cid<sup>b</sup>, O. Moldes<sup>a</sup> and J.C. Mejuto<sup>a</sup>

a) Department of Physical Chemistry, Faculty of Sciences, University of Vigo, 32004 Ourense, (Spain)b) Chemistry Department, REQUIMTE-COFB, New University of Lisbon, 2829-51-6 Monte da Caparica, (Portugal)

#### Abstract

A study of the effect of sodium bis(2-ethylhexyl)sulfosuccinate/isooctane/water microemulsions upon the stability of 3-(3,5-dichlorophenyl)-N-isopropyl-2,4-dioxoimidazolidine-1-carboxamide –iprodione– has been investigated in basic media. The presence of these microheterogeneous media implies a large basic hydrolysis of iprodione on increasing surfactant concentration and, also, on increasing water contain in the microemulsion. These results have been compared with the corresponding ones in other colloidal aggregates and with three carbamate pesticides (carbofuran, 3-hydroxy-carbofuran and 3-keto-carbofuran). In addition, it has been observed that the presence of these restricted aqueous media in the environment, in particular in watersheds and in wastewaters, could reduce significantly the half-life of iprodione.

#### Keywords

Iprodione, AOT, microemulsions, reverse micelles, surfactant, degradation, basic hydrolysis.

#### Introduction

Iprodione (IP) is an imidazole fungicide (Figure 1) used in agriculture as a contact pesticide (Cui et al., 2002; Daughtrey and Benson, 2005).



Figure 1. Structural formula of IP.



Figure 2. Structural formula of AOT.

The main mechanism inhibits the kinase protein interfering with the intracellular signals that control many cellular functions (Angioni et al, 2012; Hamada et al., 2011).

In the environment the half-life of IP is 7-60 days depending of its location, temperature, soil or pH, and the moisture content of the surrounding medium (Athiel et al., 1995). In plants, it is quickly degraded with the formation of 3,5-dichloroaniline as main metabolite, a highly nephrotoxic and carcinogenic substance (Lindh et al., 2007).

Taking account into that a large portion of chemical and biochemical processes occurs in heterogeneous media and at interfaces, the stability evaluation of xenobiotics, and in particular the IP stability in these media has significant scientific and technological interest. For this reason, it has been analysed the influence of these of one microheterogeneous media (water in oil microemulsions) upon the IP basic hydrolysis.

Microemulsions are transparent and dynamic systems with components that are auto-organized (Lindman, 1999). In the macroscopic level, these systems are isotropic dispersions of a polar compound (generally water) in an apolar medium (w/o) or vice versa (o/w) in the presence of a surfactant (presence of a cosurfactant is usually necessary to stabilize the aggregate). In the present work, we have used sodiumbis(2-ethylhexyl)-sulfosuccinate -AOT- which forms microemulsions without the presence of cosurfactants (Figure 2). It has been analysed the observed rate constant of IP hydrolysis in the presence of AOT-based w/o microemulsions in terms of kinetic models.

#### Materials and methods

All reagents used in the present study were of the maximum commercially available purity and none required further purification and supplied by Sigma-Aldrich. All kinetic tests were conducted under pseudo first-order conditions. Reactions were monitored through the first-order IP basic hydrolysis using a Varian Cary 50 Bio spectrophotometer  $(\lambda \Box \Box \Box 255 \text{nm})$ , at 25.0 ± 0.1 °C.

Microemulsions used in the present work are AOT/iC $_8/H_2O$  w/o microemulsions. In the experiments

<sup>•</sup> To whom all correspondence should be addressed: Department of Physical Chemistry, University of Vigo, 32004 Ourense, (Spain). Email: morales@uvigo.es

surfactant concentration and water contain in the microemulsion was varied. Surfactant concentration, AOT, was varied in the range [AOT]=0.10-0.70 M. The ratio  $W=[AOT]/[H_2O]$  was varied between W = 5and W=30. We must underline that W is proportional to the water pool radio, hence the size of water microdroplet was varied between  $R_{\rm h} \sim 5$ Å and  $R_{\rm h} \sim 45$ Å (which yields a water volume of  $V=2.5 \times 10^3$ – 2.0x10<sup>7</sup>Å<sup>3</sup>). The ratio  $Z=[iC_8]/[AOT]$  (which is proportional to the inverse of droplets number present in the medium) was varied between Z=6 and Z=60. Since hydrolyzation of AOT causes spectroscopic anomalous behaviours in complex reactions systems (Eastoe et al., 2006; Mao et al., 2011), the effect of AOT hydrolysis upon the IP basic hydrolysis was also investigated. Eq. (1) can be written attending to the total absorbance due to IP decomposition  $(A_{IP})$  and to the products resulting from the AOT hydrolysis ( $A_{AOT}$ ),

$$A_{t} = A_{IP} + A_{AOT} = A_{0} e^{-k_{obs}t} + A_{\infty}^{AOT} (1 - e^{-k_{AOT}t})$$
(1)

where  $A_{\infty}^{AOT}$ is the absorbance at  $t=\infty$  caused by the formation of the products resulting from the AOT hydrolysis and  $k_{AOT}$  is the pseudo-first rate constant for AOT hydrolysis reactions. The pseudo-first rate constants for AOT hydrolysis,  $k_{AOT}$ , were determined according with Eq. (1) and tend to be between  $(3.0\pm0.4)x10^{-4}s^{-1}$  and  $(1.0\pm0.2)x10^{-5}s^{-1}$  depending of the W and Z parameters of the microemulsion. These results are in good concordance with those in the literature (Leis et al., 1993; García-Río et al., 2002). In all cases the AOT hydrolysis reaction was much slower than the IP basic hydrolysis and can be assumed negligible. This result was also found for the basic hydrolysis of carbofuran and carbofuran-derivatives (Morales et al., 2012A). In addition, it is well known that the use of NaOH as additive in AOT microemulsions causes significant modifications in the internal dynamic processes, such as percolative phenomena (Arias-Barros et al., 2010; Cid-Samamed et al., 2008). These modifications influence the matter exchange between droplets of microemulsions, and therefore a kinetic effect would be only expected when the chemical reactions implied were diffusion controlled. Thus, since the alkaline hydrolysis of IP is chemical controlled, the modifications in the internal dynamic processes by NaOH could not be expected.

In order to check the IP inclusion constants in these microheterogeneous media, the partition coefficients between  $iC_8$  and water,  $K_i^w$ ,  $(K_i^w = K_{oi}/K_{wi})$  was calculated by spectroscopic methods and described elsewhere (Morales et al., 2012A).  $K_i^w$  value of 0.78 ± 0.02 was determined directly –Eq. (2)–.

$$K_{i}^{w} \cong \frac{\chi_{IP}^{water}}{\chi_{IP}^{iC_{8}}} \cong \frac{(n_{IP})_{water}}{(n_{IP})_{iC_{8}}} / \frac{n_{water}}{n_{iC_{8}}}$$
(2)

where  $\chi_{\rm IP}$  is the molar fractions of IP in each solvent and  $n_{\rm IPs}$ ,  $n_{\rm water}$  and  $n_{\rm isooctane}$  the number of moles of IP, water and  $iC_8$ , respectively.

#### **Results and discussion**

The bimolecular rate constant in water solutions has been obtained to ensure good consistency in the evaluations of the experimental results (Figure 3). In fact, this value is in good accordance as other reported previously (Morales et al., 2013). The rate constant was  $k_w=32 \pm 3 \text{ M}^{-1}\text{s}^{-1}$ .



Figure 3. Influence of [NaOH] on the pseudo-first order rate constants of IP basic hydrolysis in water.

As quoted above, to analyse the influence of microemulsion composition upon the IP basic hydrolysis, AOT concentration, W and Z have been varied In all cases, [IP] was kept constant and equal to  $5.0 \times 10^{-5}$ M. Values of [NaOH] were  $1.00 \times 10^{-3}$ M,  $1.67 \times 10^{-3}$ M and  $2.12 \times 10^{-3}$ M, which allow us to obtain the apparent bimolecular rate constant in microemulsions according to Eq. (3).

$$\boldsymbol{k}_{obs} = \boldsymbol{k}_{app} [OH^{-}]_{t} \quad (3)$$

where  $k_{obs}$  is the pseudo-first order rate constant,  $k_{app}$  the apparent bimolecular rate constant and  $[OH^-]_t$  is the total concentration of NaOH added to the reaction media.

Figures 4 and 5 show the influence of [NaOH] upon the IP hydrolysis at [AOT] constant and, at *W* constant, respectively. These results imply an inhibition of 475 and 36 times-fold, respectively. This large inhibition means that a large amount of IP will be solubilized in the apolar domain of the microemulsion. To explain this behaviour the influence of microemulsion composition must be analysed. As a result, we find a large inhibition of basic hydrolysis of the IP on increasing microemulsion water contain, as witnessed by the previous figures. An increase of 6 times the water contains in the microemulsion, keeping [AOT] constant, yields 12 times fold of inhibition in the apparent rate constant (Figure 6). We must

underline that W value is related to the microdroplet size in the microemulsion.



Figure 4. Influence of [NaOH] on the pseudo-first order rate constants of IP basic hydrolysis in the presence of AOT/iC<sub>8</sub>/H<sub>2</sub>O microemulsions.
[AOT]=0.50 M; (●) W=5, (○) W=7, (▼) W=9, (△) W=18, (■) W=25.



Figure 5. Influence of [NaOH] on the pseudo-first order rate constants of IP basic hydrolysis in the presence of AOT/iC $_{\ast}/H_2O$  microemulsions. W=22.2 M; ( $\bullet$ ) [AOT]=0.1 M; (O) [AOT]=0.2 M; ( $\blacktriangledown$ ) [AOT]=0.4 M; ( $\bigtriangleup$ ) [AOT]=0.6 M; ( $\blacksquare$ ) [AOT]=0.7 M.



Figure 6. Influence of W on the apparent bimolecular rate constant of IP basic hydrolysis in the presence of

#### $AOT/iC_8/H_2O$ microemulsions. [AOT]=0.5 M.

On increasing [AOT], at constant W, an inhibition was also observed, but in this case the decrease in the apparent bimolecular rate constant is sharp. In fact, an increase of 7 times of [AOT] yields an inhibition of 2.4 times. Figure 7 shows the influence of [AOT] upon the apparent bimolecular rate constant at W=22.2.

Table 1. Effect of different microheterogeneous media upon the basic hydrolysis of different pesticides.

Media	Р	Kinetic effect	Times-fold
AOT/iC <sub>8</sub> /H <sub>2</sub> O	IP	Large inhibition	~475
AOT/iC <sub>8</sub> /H <sub>2</sub> O	CF	Catalysis	~10
AOT/iC <sub>8</sub> /H <sub>2</sub> O	3HCF	Catalysis	~2
AOT/iC <sub>8</sub> /H <sub>2</sub> O	3KCF	Inhibition	~50
LTABr	CF	Catalysis	~5
TTABr	CF	Catalysis	~25
CTABr	CF	Catalysis	~40
Brij-35	CF	Inhibition	~2
Brij-35	3HCF	Inhibition	~3
Brij-35	3KCF	Inhibition	~2
Brij-58	CF	Inhibition	~2
Brij-58	3HCF	Inhibition	~2
Brij-58	3KCF	Inhibition	~2
Brij-78	CF	Inhibition	~2
Brij-78	3HCF	Inhibition	~2
Brij-78	3KCF	Inhibition	~3
SdS	CF	Inhibition	~6
SdS	3HCF	Inhibition	~3
SDS	CF	Inhibition	~8
SDS	3HCF	Inhibition	~4
SUS	CF	Inhibition	~7
SoS	3HCF	Inhibition	~3
STS	3HCF	Inhibition	~6
SCS	3HCF	Inhibition	~7
SOS	3HCF	Inhibition	~8
Humates	IP	Inhibition	~2
Humates	CF	No effect	-
Humates	3HCF	Inhibition	~1.7
Humates	3KCF	Inhibition	~1.5

The large inhibition, in the range 36-475 times-fold, is due to a reactive compartmentalisation. Water in oil microemulsions is an effective inhibitor of IP basic hydrolysis. Note that this large inhibition was not found in previous results (Morales et a., 2012A) with other pesticides as carbofuran and carbofuran derivatives (3-hydroxy-carboran and 3-ketocarbofuran). In our research group the influence of different micellar aggregates (Arias et a., 2005; Astray et al., 2011A; Astray et al., 2011B; Morales et al., 2012B) upon the basic hydrolysis of different pesticides has been carried out. Values of inhibition/catalisys are shown in Table 1.



Figure 7. Influence of [AOT] on the apparent bimolecular rate constant of IP basic hydrolysis in the presence of AOT/iCs/H<sub>2</sub>O. W=22.2 M.

#### Conclusions

Taking into account that an important part of soils are colloids, the possibility of the presence of restricted water environments implies that soil composition and its structure will play an important role in the stability of this fungicide. In fact, it has been observed that the presence of these restricted aqueous media in the environment, in particular in watersheds and wastewaters, could reduce significantly the halflife of this pesticide

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# **REACTION OF OH RADICALS WITH SMALL OXYGENATES IN** THE GAS PHASE: KINETIC STUDY AT ULTRA-LOW **TEMPERATURES**

M. Antiñolo<sup>1,2</sup>, E. Jiménez<sup>\*,1,2</sup>, B. Ballesteros<sup>1,2</sup>, André Canosa<sup>3</sup>, and José Albaladejo<sup>1,2</sup>

<sup>1</sup> Universidad de Castilla-La Mancha – Departamento de Química Física. Facultad de Ciencias y Tecnologías Químicas. Ciudad Real, 13071 Spain

<sup>2</sup> Universidad de Castilla-La Mancha – Instituto de Investigación en Combustión y Contaminación Atmosférica.

Ciudad Real, 13071 Spain

<sup>3</sup> Institut de Physique de Rennes – Département de Physique Moléculaire.

Rennes Cedex, 35042 France

#### Abstract

Up to now, more than 180 chemical species (molecules, ions and radicals) have been detected in the interstellar medium (ISM). In order to interpret the observed abundances, astrochemical modelling requires the knowledge of the rate coefficients (k) in the gas phase and dust grains for the potential formation and depletion processes of each species. For most gas-phase reactions, k is not known at the temperatures prevailing in the dense molecular clouds in the ISM (ca. 10 K). The aim of this work is to provide new experimental kinetic data for the gas-phase reactions of OH radicals with ethanol and acetone at temperatures typical in the ISM. A CRESU apparatus operated in pulsed mode was used to achieve (22.4±1.4) K in the uniform supersonic jet (total gas density  $n=(1.7\pm0.16)\times10^{17}$  cm<sup>-3</sup> of He), and in continuous mode to get a jet temperature of  $(61\pm1)$  K ( $n=(2.02\pm0.10)\times10^{16}$  cm<sup>-3</sup> of N<sub>2</sub>). OH radicals were generated by pulsed laser photolysis of H<sub>2</sub>O<sub>2</sub> at 248 nm and were detected and monitored as a function of reaction time by laser induced fluorescence at ca. 310 nm.

#### Keywords

OH Radical, Ultra-low Temperature Kinetics, Interstellar Medium (ISM).

#### Introduction

More than 180 chemical species have been detected up to now in the interstellar medium (ISM). Among them, there are molecules, ions and radicals, such as hydroxyl (OH) radicals that were first detected in Cassiopeia A by Weinreb et al. (1963). More recently small oxygenates, ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) such as and acetone (CH<sub>3</sub>C(O)CH<sub>3</sub>), have been first identified in Sagittarius B2 with column densities of  $10^{15}$  and  $5 \times 10^{13}$  cm<sup>-2</sup>, respectively (Zuckerman et al., 1975; Combes et al., 1987). The knowledge of rate coefficients (k) for the potential formation and depletion processes of each species is important for gas-phase astrochemical models, which are used to interpret the observed abundances. In dense molecular clouds of the ISM, temperatures can reach 10 K, and at this ultra-low temperature k values are not known for most gas-phase reactions. Usually, k values used in modelling the observed abundances are estimates, either k determined at 300 K, if no T-dependence of k is available, or extrapolations from temperature dependences reported at T > 200 K. Particularly, the last method is not valid for many radical-molecule reactions due to the observed enhancement of k at low T.

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For the reaction of OH radicals with CH<sub>3</sub>CH<sub>2</sub>OH, Caravan et al. (2014) determined k at temperatures ranging from 54 to 106 K, and at different gas densities  $((0.44-2.60) \times 10^{17} \text{ cm}^{-3})$ . In a different study, (Shannon et al., 2014) they measured k for the reaction between OH and CH<sub>3</sub>C(O)CH<sub>3</sub> between 63 and 148 K and between 3.2 and  $26 \times 10^{16}$  cm<sup>-3</sup>. In both cases, they used a pulsed Laval nozzle apparatus.

In this work we provide new experimental kinetic data for gas-phase reaction between OH radicals and ethanol and acetone at  $22.4\pm1.4$  and  $61\pm1$  K. These *k* have been determined with a pulsed CRESU apparatus (French acronym for Cinétique de Réaction en Ecoulement Supersonique Uniforme, that stands for Reaction Kinetics in Uniform Supersonic Flow) and the Pulsed Laser Photolysis (PLP) coupled with Laser Induced Fluorescence (LIF) technique.

#### **Experimental Set-Up**

The pulsed CRESU employed in the kinetic measurements is based in an aerodynamic chopper which has been recently described in detail by Jiménez et al. (2015). In Figure 1 a scheme of the setup is depicted. The stainless steel chamber (2 m long, 500 mm dia.) is connected to a compact pumping system to achieve low pressure ( $P_{cham}$  is 0.62 mbar for He and  $P_{\text{cham}} = 0.184$  mbar for N<sub>2</sub>). A movable gas expansion

<sup>\*</sup> To whom all correspondence should be addressed (Elena.Jimenez@uclm.es)

system is placed inside the chamber to generate a cold uniform supersonic jet. The expansion from a reservoir (V = 12 L,  $P_{res}$  = 337 mbar of He or  $P_{res}$  = 41.7 mbar of  $N_2$ ), where the gas flows through at a constant flow rate at room temperature, to the low pressure region is occurring through a convergent-divergent nozzle (throat diameter = 3.4 mm). During the expansion, the gas mixture (mainly He) is pulsed at 10 Hz by means of a stainless steel rotary disk (aerodynamic chopper) with two symmetrical apertures (Jiménez et al. 2015). Under these conditions, the achieved temperature in the uniform supersonic jet is 22.4±1.4 K and the total gas density  $n=(1.7\pm0.16)\times10^{17}$  cm<sup>-3</sup>. When this apparatus is operated in continuous mode using N<sub>2</sub> as a carrier gas, a temperature of  $61\pm1$ iet Κ is obtained  $(n=(2.02\pm0.10)\times10^{16} \text{ cm}^{-3})$ . Pitot measurements were performed to obtain the spatial profiles of T and n in both operating conditions.



Figure 1. Schematics of the experimental set-up used in this work.

from a transmission The signal optocoupler synchronizes the exit of photolysis and probe lasers through the apertures. OH radicals are generated by PLP of H<sub>2</sub>O<sub>2</sub> using a KrF excimer laser ( $\lambda = 248$  nm). They are detected by LIF by exciting them with a collinear 282 nm radiation from a frequency-doubled dye laser pumped by a XeCl excimer laser ( $\lambda = 308$  nm). LIF signal is collected as a function of reaction time by a photomultiplier tube by means of an optical lenses system. At short reaction times (tens of µs), the LIF signal from excited OH increases due to rotational relaxation. In the analysis of the OH temporal profiles, only the decay of the LIF signal at  $t > 50 \,\mu s$  is considered. The observed loss of OH radicals is due to reaction with reagent (acetone R1 or ethanol R2), with the OH precursor (R3) or other losses (R4), such as diffusion or reaction with impurities:

 $OH + CH_3C(O)CH_3 \rightarrow Products$  (R1)

 $OH + CH_3CH_2OH \rightarrow Products$  (R2)

 $OH + H_2O_2 \rightarrow H_2O + HO_2 \tag{R3}$ 

 $OH \rightarrow Other Losses$  (R4)

Under pseudo-first order conditions, the rate coefficients, k', for a given reactant concentration, [R], are obtained from the analysis of the exponential decays (see Figure 2).



Figure 2. Examples of the temporal profile of the LIF signal in the reactions between OH and acetone  $([R] = 2.18 \times 10^{13} \text{ cm}^{-3})$  or ethanol  $([R] = 1.16 \times 10^{13} \text{ cm}^{-3})$  at ca. 23 K.

Varying the concentration of reactant and maintaining the pseudo-first order conditions and the OH-precursor concentration constant, k' is linearly related to [R]:

$$k' = k_0 + k_{\rm OH}(T)[R]$$
(E1)

where  $k_0$  is the measured rate coefficient k' in the absence of R (R3 and R4). The second order rate coefficient at a given temperature, k(T), is obtained from the slope of the plot of k' as a function of [R]. In order to compare all experiments, k' is corrected with  $k_0$  as:

$$k' - k_0 = k_{\text{OH}}(T)[\mathbf{R}] \tag{E2}$$

Some examples of plots of  $k'-k_0$  versus [R] are shown in Figures 3 and 4 for the reaction between OH radicals and acetone and ethanol, respectively, at ca. 23 K and 61 K.

As can be seen in Figs 3 and 4, a deviation of Eq. (2) is observed at high concentrations. This curvature has been attributed to an overestimation of the reactant concentration, i.e. the "real" concentration is lower due to the formation of complexes. Only data fitting Eq. (2) were considered in the data analysis.



Figure 3. Variation of  $k^{2}$ - $k_{0}$  versus acetone concentration. Lines represent the fit to Eq. (2).



Figure 4. Variation of  $k' \cdot k_0$  versus ethanol concentration. Lines represent the fit to Eq. (2).

#### **Results and Discussion**

The values of  $k_{OH}(T)$  determined in this work are summarized in Table 1. Our results follow the same trend of previous studies, the rate coefficient is greatly enhanced at ultra-low temperatures compared to room temperature rate coefficients.

 Table 1. Rate coefficients for reactions R1 and R2
 obtained in this work.

Reagent	<i>T /</i> K	<i>k</i> <sub>OH</sub> ( <i>T</i> )/ 10 <sup>-10</sup> сm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>
CH <sub>3</sub> C(O)CH <sub>3</sub>	22.4±1.4	$1.45 \pm 0.10$
	61±1	$1.00\pm0.03$
CH <sub>3</sub> CH <sub>2</sub> OH	$22.4{\pm}1.4$	$1.58 \pm 0.06$
	61±1	0.741±0.019

These results are compared with previous studies in Figures 5 and 6, where a "U shape" behavior

is observed in both cases for the log k versus T plot. At temperatures between 300 and 800 K, a positive T-dependence of k was reported in the literature. While at temperatures below 200 K, a negative temperature dependence is observed. In fact, when comparing k(300K) with k(23K), an increase of several orders of magnitude is observed (3 for acetone and 2 for ethanol). Shannon et al. (2013) also observed this behavior in the reaction between OH and methanol, and they attributed it to the formation of a hydrogen-bonded complex that is sufficiently long-lived to undergo quantum-mechanical tunneling to form products.



Figure 5. Temperature dependence of k for the reaction  $CH_3C(O)CH_3 + OH$ .



Figure 6. Temperature dependence of  $k_{OH}(T)$  for the reaction  $CH_3CH_2OH + OH$ .

Shannon et al. (2014) and Caravan et al. (2014) have shown that there is a pressure dependence of  $k_{OH}(T)$  for reactions R1 and R2 between  $4 \times 10^{16}$  cm<sup>-3</sup> and  $2.6 \times 10^{17}$  cm<sup>-3</sup> in N<sub>2</sub>. In Figures 5 and 6 all data from Shannon et al. (2014) and Caravan et al. (2014) are shown.

For acetone, the pressure dependence of  $k_{OH}(T)$  at 80 K is much less pronounced than that observed at 140 K, and it could be within the experimental uncertainties. In fact, our results for acetone and ethanol

at 61 K are in reasonable agreement with those from Shannon et al. (2014) at 80 K and Caravan et al. (2014) at 63 K.

#### Conclusions

Reactions between OH and acetone and ethanol at ultra-low temperatures are much faster than estimated by Arrhenius equations obtained at temperatures above 200 K. This shows that it is extremely important to measure rate coefficients at temperatures below 200 K, due to the application that these data may have in astrochemical models.

The comparison between this work and previous studies has pointed out the necessity of more measurements at different gas densities and temperatures.

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# Mechanistic role of the second and third coordination sphere of cysteine dioxygenase

<u>Casey G. Davies</u><sup>1,2</sup>, Egor P. Tchesnokov<sup>1</sup>, Matthias Fellner<sup>1</sup>, Sigurd M. Wilbanks<sup>2</sup> and Guy N. L.

Jameson<sup>1</sup>

Departments of Chemistry<sup>1</sup> and Biochemistry<sup>2</sup>, University of Otago, PO Box 56, Dunedin 9054 New Zealand

Cysteine dioxygenase (CDO) is а non-heme mononuclear iron enzyme which catalyses the first step of oxidative cysteine metabolism by oxidising cysteine to cysteine sulfinic acid. Oxidation takes place at the iron centre which is in close proximity to the sidechains of residues cysteine 93 and tyrosine 157. C93 and Y157 can form a thioether crosslink which is observed in both recombinant CDO and CDO derived from rat liver lysate. Not all protein contains the crosslink and it has been shown previously that the rate of multiple turnover reaction depends upon the fraction of crosslink.<sup>1,2</sup> However, bacterial CDOs are unable to form this crosslink because glycine is highly conserved at an equivalent position to cysteine 93. This shows that the crosslink is not a prerequisite for catalysis. Recent



Figure. Active site of Cysteine dioxygenase showing the hydrogen bonding network and interactions with bound substrate.

studies using variants of rat CDO where C93 had been substituted by alanine have suggested a relationship between  $k_{cat}$  and the crosslink.<sup>3</sup> To further assess this relationship , we produced a C93G variant of rat CDO which converts rat CDO into a bacterial-type CDO.<sup>4</sup> Crystallographically, we could show that there were no large structural rearrangements. Spectroscopic and kinetic data using Mössbauer spectroscopy, HPLC and a chromogenic assay<sup>5</sup> showed that this enzyme efficiently forms a catalytically competent *ES* complex with cysteine and turns over. Michaelis-Menten kinetics have shown that the C93G variant is just as active as wild-type but with a shift in the pH optimum.<sup>4</sup>

This work has now been expanded to include other variants that allow us to probe the other component of the crosslink, tyrosine (Y157F) or a highly conserved histidine involved in a hydrogen bonding network to the tyrosine (H155Q). Results suggest the presence of two ionisable groups in the active site that are responsible for activity of cysteine dioxygenase. The identities and potential roles of these groups will be discussed.

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# Green Chemistry in Oxidation: Catalytic Activation of Hydrogen Peroxide by Transition on metals for Oxidation Reactions

Ahmad M. Al-Ajlounia and Reem Marjib

<sup>a</sup>Basic Sciences Department, College of Science and Health Professions, King Saud bin Abdulaziz University for Health Sciences, Riyadh 11481, Kingdom of Saudi Arabia. Email: <u>ajlounia@ksau-hs.edu.sa</u> <sup>b</sup>Department of Chemical Science, Jordan University of Science and Technology, Irbid 22110, Jordan

#### Abstract

Catalytic activation of hydrogen peroxide in water is of greatest environmental importance. We have been working on the catalytic activation of peroxides by transition metal catalysts toward oxidation of organic and inorganic substrates. Different Mo(VI), W(VI) and Mn(III) complexes are under investigation in our laboratory. We have prepared and design series of Mo(VI) and Mn(III) Schiff-base catalysts and studied their activity in oxidation of organic substrates by peroxides, such as epoxidation. Detail kinetic and mechanistic studies are all carried out in order to understand the role of the catalyst and the effect other variables, such as concentrations, solvent and temperature, on the reaction. We have found that the metal activates the peroxide by forming a metal-peroxo species, which is able to transfer an O atom to the organic substrate, as shown below. It has been demonstrated that the presence of electron-withdrawal group(s) on the metal catalyst enhances its activity.

Keyword: Kinetic Study, Oxidation, Metal Peroxides, Catalytic, Green Chemistry

#### Introduction

Oxidation, in general, is very important chemical process in synthesis of fine chemicals and industrial compounds. Naturally, oxidations carried out by molecular oxygen and hydrogen peroxides are crucial for biological systems and these processes are catalyzed by enzymes, such as peroxidases. The active sites of these enzymes contain transition metals, such as Fe, Mn and Mo. (Brink etal., 2004) Researchers and industries have been searching for suitable oxidants (catalytic or noncatalytic) that are available, cheap, stable, active and environmentally acceptable. Recently, the environmental issues have taken a great attention due to many environmental concerns and legislations that enforce waste removal and clean up at the end of the process which makes the process very costly. Therefore, finding environmentally safe oxidant (produce safe byproducts) has become a challenge for researchers in this field. (Liao etal., 2012) The best oxidant is oxygen, due to high oxygen content (100%), available everywhere, cheap and produces water. Nevertheless, oxygen is thermodynamically excellent oxidant, kinetically is not reactive due to the formation of high energy radical intermediates (such as OH radical) through a 4-electron reduction of O<sub>2</sub> to H<sub>2</sub>O, and can hardly be activated. Hydrogen peroxide, is considered as the second best oxidant. The oxygen content is almost 50% (by mass) of O2 and produces water upon reduction. Hydrogen peroxide (Mr. Clean) is amphoteric, and can be activated by acidic and basic catalysts. It is also very attractive because its solubility in water and many organic solvents is quite large. As a result, oxidation systems that use hydrogen peroxide in conjunction with catalytic amount of cheap, relatively non-toxic metals such as iron, molybdenum and

manganese, are highly desired for application in many industrial areas.

Many transition metals, such as Mo(VI), W(VI), Re(VII), are acidic catalysts that activate hydrogen peroxides toward many oxidation processes. Epoxidation of olefins to form epoxides is the most important oxidation process in industries because epoxides find many applications in polymer industries. We have been conducting research in investigating the kinetics and mechanisms of activation of peroxides by Mo(IV), W(VI) and Re(VII) catalysts, such as polyoxometallates of Mo and W. and methyltrioxorhenium(VII). (Kuhn etal., 1994 and Al-Ajlouni etal., 2009) Over 15 years in this field we have proposed tens of catalytic reaction mechanisms after detail kinetic studies, discovered and modified many catalytic systems, and find out the optimum conditions for better catalytic activity. (Al-Ajlouni etal., 2008) In this work, we have investigated the catalytic activity of Mn and Mo complexes with N and or O bases toward peroxide activation. Manganese and molybdenum are cheap, available and stable metals. Their compounds (as potential catalysts) are easily prepared directly from their salts or aqua ions, and can be recycled. In a previous study, we found that imidazole and other aromatic amines enhances the catalytic activation of some Mn salts and Re(VII) toward oxidations with hydrogen peroxide. This work will focus on Mn and Mo Schiff base complexes and study their catalytic activities in the presence and absence of N-base ligands such as imidazoles.

# Part I: Ligands and Complexes Preparation, and Characterization

In this part, we have followed literture prucedures with some modifications to prepare the ligands and the complexes. (Martinez etal., 2005) We started the work by preparing the first part of the macrocyclic Schiff bases (o-hydroxobenzaaldehyde derivatives) followed by adding the primary bidentate amine as shown in Schemes I. The Schiff bases were fully characterized by spectroscopic methods, such as UV-vis, IR and NMR spectroscopic techniques, and elemental analysis prior to complexation with the Using similar identification metal ion. and characterization methods, the complexes were fully characterized and their structures have been confirmed. The chloride complexes of Mn(III) were prepared by adding manganese(III) acetate and NaCl to the Schiff base solution in ethanol (Scheme I). The Mo(VI) complexes were prepared by adding MoO<sub>2</sub>Cl<sub>2</sub> to the prepared Schiff bases, as shown in Scheme II. We have varied the X group on the ligand by using different derivatives of benzaldehyde. Electrondonating (CH<sub>3</sub>) and electron-withdrawing (NO<sub>2</sub>) groups have been utilized in order to investigate the electronic effect on the complexes' features and catalytic activities.



Scheme I. Preperation of the salen Shiff base and formation of Mn(III)-salen complexes;  $X = CH_3$  or  $NO_2$ .

#### Part II- Kinetic Studies:

#### A. The Catalytic Activities.

We have tested the catalytic activities of two Mn(III) and two Mo(VI) complexes. The effect of electron-donating (CH<sub>3</sub>) and withdrawing (NO<sub>2</sub>) groups had been investigated. The presence of electron withdrawing group enhances the catalytic activities of both metals toward epoxidation of b-methoxystyrene and diphenyl sulfide by hydrogen peroxide.



Scheme II. Preperarion of the Mo(VI)-salen complexes; X = CH<sub>3</sub> or NO<sub>2</sub>

Figures 1 and 2 show that the reaction rate constants of Mn and Mo catalysts vary linearly with the catalyst concentrations indicating that the catalytic rates are first-order with respect to [catalyst]. Indeed, plots of  $log(k_{obs})$  against log[catalyst] were linear with slopes very close to one.



Figure 1. Variation of the rate constant with the catalyst concentration for the epoxidation of  $\beta$ -methoxystyrene by  $H_2O_2$  as catalyzed by Mn(III)-salen complexes at 40 °C.



Figure 2. The rate constant dependence on the catalyst concentration for the epoxidation of  $\beta$ -methoxystyrene by  $H_2O_2$  as catalyzed by Mo(VI)-salen complexes at 40 °C.

#### B. Effect of N-base Ligands

Kinetics studies have been carried out on the epoxidation of  $\beta$ -methoxystyrene by H<sub>2</sub>O<sub>2</sub> as catalyzed by the Mn(III)-salen complexes attached to a nitro or a methyl groups. The investigations were carried out in the absence of a N-base ligands and in the presence of different bases of pyridine and imidazoles (pyridine, 3-cyanopyridine, imidazole and N-methylimidazole), see Figure 3. The catalytic activities of the Mn(III)-salen have been increased in the presence of all the N-bases. However, imidazoles enhance the activity more than the other pyridine bases.

A similar effect of the N-base ligands on the reaction rates of the Mo(VI) complexes was found, see Tables 1 and 2. In case of the Mo(VI) complexes however, the effect of imidazole and the other N-bases on the catalysts' activities was more than their effects on the Mn(III) catalysts. This is due to the high acidity of Mo(VI) relative to that of Mn(III) which is reflected on the high affinity of the Mo complexes to the N-base ligands.



Figure 3. Variation of the observed rate constant with the N-base effect for the epoxidation of  $\beta$  -methoxystyrene by  $H_2O_2$  as catalyzed by Mn(III)-salen complexes at 40 °C.

These results indicate that the N-base ligands have direct influence on the metal center rather than just increase the media pH due to their basicity. In other words, the N-donor ligand coordinates to the metal center before the activation of peroxide step takes place. In the light of these kinetic data, the following mechanistic steps have been proposed:



Scheme III. Proposed mechanism for the complexation of Mo(VI) and Mn(III) complexes with the N-base followed by activation of hydrogen peroxide toward oxidation of an organic substrate (S).

The coordination of peroxide onto the metal (as shown in Scheme III) is more likely to occur in case of Mn(III) due to the presence of the vacant site on the penta coordinated Mn(III)-salen-N-base, or by replaying the labile Cl ligand. For Mo(VI) complex, hydrogen peroxide replaces the oxo with a peroxo group, as shown below:



Many compounds and active intermediates of Mo(VI) with bidentate peroxo ligands are known and identified.

Table 1. The catalyzed and the uncatalyzed rate constants for the epoxidation of  $\beta$ -methoxystyrene with hydrogen peroxide as catalyzed by Mn(III) catalysts in the presence and absence of imidazole at 40 °C.

Catalyst	Mn(III)	Mn(s on	Mn(salen) only		Mn(salen) + Imidazole	
		X = CH3	X = NO2	X = CH3	X = NO2	
k <sub>cat\ M</sub> <sup>-1</sup> s <sup>-1</sup>	0.0012	0.27	0.39	0.45	0.65	
kuncat\10 <sup>4</sup> s <sup>-1</sup>	1.32	1.46	1.66	1.76	1.96	

Table 2. The catalyzed and the uncatalyzed rate constants for the epoxidation of  $\beta$ -methoxystyrene with hydrogen peroxide as catalyzed by Mo(VI) catalysts in the presence and absence of imidazole at 40 °C.

Catalyst	MoO2Cl2	2Cl2		Mo(salen) + Imidazole	
		X = CH3	X = NO2	X = CH3	X = NO2
kcat\ M <sup>-1</sup> s <sup>-1</sup>	0.014	3.5	4.5	7.6	10.8
$k_{uncat \setminus 10^3 s^{-1}}$	1.32	1.3	1.2	5.1	5.8

#### C. The Rate Law.

The kinetic studies involved oxidation of organic substrate, such as olefins and sulfides, by hydrogen peroxide as catalyzed by the Mn- and Mo-Schiff bases complexes prepared in this work. In order to investigate the reaction mechanisms, detail kinetic studies have been carried out on both metal catalysts. We have found that all reactions are first order with respect to the catalyst concentration. The dependence of the initial rate on the oxidizing agent  $(H_2O_2)$  was carried out in mixed CH<sub>3</sub>CN/H<sub>2</sub>O (8:2) solutions. When the concentrations of the olefin and the catalyst were held constant at 1.0 mM each, the rate was found to be first-order with respect [H<sub>2</sub>O<sub>2</sub>] at low concentration ( $[H_2O_2] < 2 \text{ mM}$ ) and becomes less than  $1^{st}$  order at higher concentration. At very high [H<sub>2</sub>O<sub>2</sub>] (> 30 mM), the reaction is independent on  $[H_2O_2]$ (i.e. zero-order), see Figure 4.

Figure 4. A plot of the initial rate of oxidation of  $\beta$ methoxystyrene (2.0 mM) by H<sub>2</sub>O<sub>2</sub> catalyzed by the Mo-NO<sub>2</sub> catalyt (1.0 mM) against [H<sub>2</sub>O<sub>2</sub>] in CH<sub>3</sub>CN/H<sub>2</sub>O (8:2 v/v) at 40 °C.

A very similar trend, as shown in Figure 4, was observed for the dependence of the initial rate on the substrate ( $\beta$ -methoxystyrene) concentration. The kinetic data obtained from variation of the initial rate with [H<sub>2</sub>O<sub>2</sub>], Figure 4, and with [olefin] were fit very well to the following rate law, which is derived based on the proposed mechanism shown in Scheme III. A similar mechanism and rate law is reported for the activation of hydrogen peroxiede by other Mo(VI) catalysts toward oxidation of olefins and sulfides<sup>3-5</sup>.

 $Rate = rate_{uncat} + rate_{cat}$ 

rate<sub>cat</sub> = 
$$\frac{k_1[H_2O_2][cat]_T[olefin]}{k_1 + k_2[H_2O_2] + k_3[olefin]}$$
 (Eq. 2)

The above rate law equation summarize the dependence of the rate on all concentrations involve in the reaction in the absence of the N-base. A separate treatment in the presence of imidazole show that when imidazole present in concentrations at least 5 times more than the catalyst concentration, the catalyst completely coordinates to imidazole. In other words, one can simply apply the same rate law shown in Eq. 2 by just replacing  $[cat]_T$  with  $[cat-Im]_T$ , where  $[cat]_T$  is the total concentration of the catalyst in the absence of imidazole and  $[cat-Im]_T$  is the total concentration of the catalyst in the initial concentration of the catalyst.

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## THE KINETICS AND MECHANISM OF THE OXIDATION OF BRILLIANT GREEN BY CARBONATE ION IN THE PRESENCE OF SOME CATIONIC SURFACTANTS

Soriyan Oladega O<sup>\*</sup>, Ogunlusi Grace.O, Owoyomi Olanrewaju and Adegoke Adedotun Department of Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria

#### Abstract

The oxidation of Brilliant green by carbonate ion was studied in aqueous solution of dodecyl trimethylammonium bromide (DTAB), tetradecyltrimethylammonium bromide (TTAB), cetyltrimethylammonium bromide (CTAB) hexadecylpyridinium bromide (C<sub>16</sub>PBr), and hexadecyltriphenylphosphonium bromide (C<sub>16</sub>TPPBr) at 25°C. The pseudo-first order rate constant variation with surfactant concentration shows a sigmoid shaped curve which is analogous to positive co-operativity in enzymatic reaction. The catalytic factor of the surfactants ( $k_{\varphi}/k_w$ ) on the reaction are 7.51, 10.14 and 18.50 in aqueous solutions of DTAB, TTAB and CTAB respectively which is consistent with the hydrophobic effect due to change in the length of the carbon chain of the surfactants. In C<sub>16</sub>PBr, CTAB and C<sub>16</sub>TPPBr the catalytic factor are 23.40, 18.50 and 4.02 respectively. This can be explained to be due to modification in the head groups of the surfactants and the competition between electrostatic and hydrophobic effects of the carbonate ion and brilliant green for the cationic surfactant. The data obtained fit the pseudophase model of micellar catalyzed reaction.

Keywords: Brilliant green, catalytic factor, hydrophobic effect, pseudophase model

#### 1. Introduction

Synthetic dyes are a kind of organic compounds with a complex aromatic molecular structure that can brighten and firm colour to other substances. Brilliant green dye used in the investigation is a triphenyl nitrogen containing cationic dye. The use of brilliant green has been banned in many countries due to its carcinogenic nature (Au et al 1979; Thomas and MacPee, 1984). It is used as dye to colour synthetic fibers and silk, biological stain, dermatological agent, veterinary medicine, and as an additive to poultry feed to inhibit propagation of mold, intestinal parasite and fungus. These synthetic dyes and pigments are released as textile effluents on daily bases. The continuous discharge of these toxic and mutagenic dyes impose a selective pressure on the microbial flora residing in wastewater habitats. Several physicochemical methods such as adsorption, flocculation, activated carbon adsorption, reverse osmosis, biological treatment, biodegradation, chlorination, ozonation, photolysis, ion pair extraction, electrochemical treatment and redox reactions are frequently used to remove these contaminants (Banat et 1996). The alkaline fading al, of stable triphenylmethane dye is a reaction with long chemical tradition and has become a popular one for undergraduate laboratories (Audent et al, 2003). It has been found that reactions also takes place with nucleophiles other than OH<sup>-</sup>, a fact that has been used for construction of the familiarRitchie N<sup>+</sup> nucleophicity scale (Mayr et al, 2008). This present study is intended to investigate the decolourization of Brilliant Green with Carbonate ion (CO<sub>3</sub><sup>2-</sup>) in aqueous and micellar media of cationic surfactants. The interest has arisen not only from fresh opportunities both for controlling the rate of chemical reactions and studying their mechanisms but that the reaction will be studied in different organized media such as cation surfactant solution. Such organised media can produce different types of interaction with the incoming species by electrostatic, hydrophobic, and charge transfer (Fendler and Fendler, 1975; Soriyan et al, 2009). All these three interactions can play a crucial role in the altering of the reaction pathway and the rate of the reaction. The choice of the cationic surfactant is to investigate the effect of surfactant chain length and head-group modification on the rate of the reaction.

#### 2. Experimental

#### 2.1 Materials

Brilliant green (BG<sup>+</sup>) was obtained from Sigma-Aldrich Chemical Company was used without further purification. It was characterized by its UV-Visible spectrum, which gave a molar extinction coefficient of which is in agreement with the literature value (Patel and Patel, 1998)) at  $\lambda_{\text{max}}$  of 624 nm. The cationic surfactants employed in this study; Cetyltrimethyl ammonium bromide (CTAB), Dodecyl trimethylammonium bromide (DTAB) and Tetradecyltrimethylammonium bromide (TTAB) were obtained from Sigma Aldrich Chemical Company while Hexadecylpyridinium bromide  $(C_{16}PBr),$ and Hexadecyltriphenylphosphonium bromide (C<sub>16</sub>TPPBr), were purchased from Lancaster Synthesis of England. They were of the highest available purity and used as received. Their purity were ascertained by determination of the critical micelle concentration in aqueous solution at 25 °C and the values were in good agreement with the literature values (Fendler and Fendler, 1975). Analar grade Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) purchased from Sigma-Aldrich chemical company was also used without further purification. All solutions were prepared in glass distilled water.

#### 2.2 Kinetics

Kinetic data for oxidation of the brilliant green (BG<sup>+</sup>) were collected by monitoring the decrease in absorbance of the dye at the maximum absorption wavelength ( $\lambda_{max}$ of 624 nm) as a function of time using UV-Visible 1800 Shimadu Spectrophotometer fitted with thermostable cell compartment. The reaction components were calculated and mixed in 1 cm (3cm<sup>3</sup>) quartz cell, with dye being added last to ensure minimum pre-mixing reaction. All reactions were carried at  $25.0 \pm 0.1$  °C. The concentration of the Brilliant green dye was maintained at 2.0 x  $10^{-6}$  mol dm<sup>-3</sup> (0.2 absorbance) in order to avoid the complication that may arise from the dependence of the oxidation on the concentration of the dye and the carbonate ion concentration maintained at 1.0 x 10<sup>-3</sup> mol dm<sup>-3</sup>. All runs were performed pseudo first order kinetics. The observed rate constants were obtained from the slope of ln (A<sub>t</sub> - A<sub> $\infty$ </sub>) versus time where A<sub>t</sub> and  $A_{\infty}$  are the absorbance at a given time (t) and at infinity time respectively. The reaction proceeded to completion as judged from the complete fading of the dye at the end of the reaction.

#### 3. Results and Discussion

# 3.1 Dependence of the observed rate constant on the surfactant concentration

The variation of the observed rate constant,  $k_{obs}$  with surfactant concentrations of Dodecyl trimethyl Ammonium Bromide (DTAB), Dodecyl trimethyl Ammonium Bromide (DTAB), Tetradecyltrimethyl Ammonium Bromide (TTAB) and Cetyltrimethyl

ammonium bromide (CTAB) as shown in figure 1. The concentration of carbonate ion was kept constant at 1.0 x 10<sup>-3</sup> mol dm<sup>-3</sup> for each of the run in all the surfactants used. The  $k_{obs}$  – [Surfactant] profiles are structured. At low [Surfactant] there is little or no change in the observed rate constant, beyond which there is rapid change in  $k_{obs}$ , approaching saturation at concentration greater than the critical micelle concentration (cmc). This observation is due to the dye- surfactant monomer interaction with the formation of dye-surfactant aggregrates of varying sizes made up of few monomers (dimer, trimer,s etc.), a phenomenon that has been observed in many systems ( refs). Hence the structure of  $k_{obs}$  – [Surfactant] (figure 1) is associated with dyesurfactant aggregates in different stages of micellar evolution. The maximum catalytic factor which is ratio of rate constants in micelle and in aqueous media  $(k_m/k_w)$  is 7.5, 10.1 and 18.5 for DTAB, TTAB and CTAB respectively (Table 2). Catalysis is observed in all the surfactants used in this work because the substrate, brilliant green (BG) and the nucleophile (carbonate ion) are attracted to the micellar surface with different partition constants basesd on electrostatic and hydrophobic consideration. A comparative analysis of the three surfactants use in this work show that the rate of oxidation of Brilliant green (BG) increases with increase in chain length of the cationic surfactants (figure 1). For example: Rate (DTAB) < Rate (TTAB) < Rate (CTAB). This is an indication that the substrates are more reactive when the micelles are formed from more hydrophobic surfactants which is in agreement with the observation of earlier workers ( Ige and Soriyan,1986).

The two surfactants have the same chain length of  $C_{16}$  but different head group. The  $k_{obs}$  – [Surfactant] profiles of the two surfactants show similar structure.



Figure 1: The plot of  $k_{obs}$  – [Surfactant] for the three surfactants: CTAB, TTAB and DTAB.

The results of observed  $k_{obs}$  – [Surfactant] profiles for hexadecylpyridinium bromide (C<sub>16</sub>PyBr) and hexadecyltrimethylammonium (CTAB) at fixed CO<sub>3</sub><sup>-</sup> ion concentration of 1.0 x 10<sup>-3</sup> mol dm<sup>-3</sup> as in other surfactants are shown in Figure 2.



Figure 2: The plot of  $k_{obs}$  – [Surfactant] for the three surfactants: CTAB and  $C_{16}PyBr$ 

The profiles show overall catalysis at all surfactant concentration. The catalytic factor  $\binom{k_{obs}}{k_w}$  is 18.59 and 23.30 in CTAB and C<sub>16</sub>PyBr respectively which is an indication that the rate of oxidation of Brilliant green increases with change in the head group. The enhancement in the rate constants at all concentration in C<sub>16</sub>PyBr compared to *CTAB* may be due to two major factors operating in the two surfactants.

- The donating effect of the electrons due to the three methyl groups attached to the positive nitrogen atom of CTAB. This reduce the effective attraction for carbonate ion to the surface of the micelle formed which in turns decreases the rate of reaction of brilliant green (BG<sup>+</sup>) with CO<sub>3</sub><sup>2-</sup> which takes place on the micellar surface when compared with C<sub>16</sub>PyBr head group.
- The rate enhancement in C<sub>16</sub>PyBr is due to the stabilization of positive charge on nitrogen atom due to the resonance effect on pyridinium group on the head of the micelle (Figure:3) The stabilization of the positive charge attract more carbonate ions to the surface of the micelle which increases the reaction rate in C<sub>16</sub>PyBr than in CTAB

These two factors are responsible for the high catalytic factor in  $C_{16}$ PyB (23.30) than CTAB (18.5).

 $k_{obs}$  – [Surfactant] profile The structure of hexadecyltriphenylphosphonium bromide (C16TPPBr) is similar to other surfactants discussed above with maximum catalytic factor of 4.02. On comparing with  $k_{obs}$  – [Surfactant] profile for hexadecylpyridinium bromide (C<sub>16</sub>TPPBr), the rate constant is strongly reduced in C<sub>16</sub>TPPBr. This reduction in quaternary phosphonium cation is due the fact that the phosphorous center bears a positive charge which is reduced drastically due to the steric effect due to three bulky phenyl groups attached to the phosphorous atom couple with the donating effect of electrons on the positive atom. The drastic reduction also reduce the carbonate ion attraction to the micellar surface and hence great reduction in catalytic factor.



**Figure 3**: Resonance stabilization of pyridine nitrogen positive charge on the surfactant

Table 2 : The maximum catalytic factors	$(k_{m}/$	$k_w$ ) of
the surfactants used		

ine Burraeta	unto used	4.			
Surfactant	DTAB	TTAB	CTAB	C <sub>16</sub> PB	C <sub>16</sub> TPPBr
Catalytic					
Factor	7.51	10.14	18.50	23.30	4.02

#### 3.2 Mechanism of the Reaction

In order to interpreate the kinetic data, the pseudo-phase separation kinetic model proposed by Menger and Portnoy (1967) was considered. The model assumes that the substrate,  $BG^+$  associates with n number of surfactant molecules D to form critical micelle  $D_n - BG^+$  which may react carbonate ion according to the following scheme:

$$BG^{+} + D_{n} \xleftarrow{\overset{R_{BG^{+}}}{\longleftarrow}} [D_{n} - BG^{+}]$$

$$BG^{+} + CO_{3}^{2-} \xleftarrow{\overset{k_{w}}{\longrightarrow}} product$$

$$\left[D_{n} - BG^{+}\right] + CO_{3}^{2-} \xleftarrow{\overset{k_{m}}{\longrightarrow}} product$$

The  $k_w$  and  $k_m$  are the second order rate constants in aqueous and micellar pseudo phase respectively while

 $K_{_{RG^{+}}}$  is the substrate-micelle binding constant.

 $\left[D_{n}\right] = \left\{ \left[\text{Surfactant}\right] - \text{cmc} \right\}$ (1)

cmc is the critical micelle concentration.

The observed rate constant  $k_{dx}$  is expressed as a function of surfactant concentration by the following equation:

$$k_{obs} = \frac{\left\{k_{w} + k_{m}K_{BG^{*}}\left[D_{n}\right]\right\}\left[CO_{3}^{2-}\right]_{w}}{1 + K_{BG^{*}}\left[D_{n}\right]}$$
(2)

The above equation predicts saturation and variance of  $k_{obs}$  at higher surfactant concentrations as we have observed in the plots of  $k_{obs}$  against  $[D_n]$  for all the surfactants used in this work. The data was curve fitted and the surfactant as the chain length increases. The trend in  $k_m$  also shows the reaction is faster in micellar phase than in the bulk water phase as the overall rate increases with increase in chain length. In comparing CTAB, C<sub>16</sub>PyBr and C<sub>16</sub>PPBr, with all having sixteen carbon chain length, the change in  $k_m$  and  $K_{BG^+}$  can only be due to the polar head group and steric hindrance due bulky group attached to the charged

surface. For CTAB and C<sub>16</sub>PyBr, the charged surface of the pyridium group the charged surface of the micelle. However drastic change in the substrate binding constant of brilliant green,  $K_{BG^*}$  in C<sub>16</sub>PPBr is

due to strong steric hindrance by the three phenyl group

using a software called 2D TableCurve 5.01 and from which we were able to obtain the kinetic parameters. A typical example of these plots is shown in Figure 4.



Figure 4: A Typical plot of  $k_{obs}$  against  $[D_n]$  for all the surfactants used.

The values of the kinetic parameters  $k_m$  and  $K_{BG^+}$  obtained for the various surfactants are shown in Table 2. From the data in Table 4, it can be seen that the binding constant of Brilliant green to the surfactant ( $K_{BG^+}$ ) increases with increase in change length of the surfactant (i.e from DTAB, TTAB to CTAB) while the rate constant in micellar phase,  $k_m$  also increases with the change length. This is an indication of strong hydrophobic interaction between brilliant green attached to the atom in hexadecyltriphenyl phosphonium bromide (C<sub>16</sub>TPPBr) couple with reduction in the charge on the head group.

 Table 2: Kinetic Parameters obtained from the Model for the oxidation of Brilliant green by carbonate ion.

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SURFACTANT	$k_m \left( dm^3 mol^{-1}s^{-1} \right)$	$K_m\left(dm^3mol^{-1}\right)$
DTAB	(1.51±0.07) x 10 <sup>-3</sup>	727.57±212.37
TTAB	(2.12±0.09) x 10 <sup>-3</sup>	1361.12±267.83
СТАВ	$(3.40\pm0.01) \ge 10^{-3}$	50992.32±300.25
$C_{16}PyBr$	$(4.31\pm0.07) \ge 10^{-3}$	39291.31±707.55
C <sub>16</sub> TPPBr	(2.79±0.85) x 10 <sup>-4</sup>	12413.75±317,79

#### 4. Conclusion

The oxidation of Brilliant Green by carbonate ion in the presence of some cationic surfactant has been studied. The observed catalysis in each of the surfactant is due to the dye-surfactant monomer interaction with the formation of dye-surfactant aggregates of varying sizes made up of few monomers. The  $k_{abs}$  – [Surfactant] profiles are structured and are associated with dyesurfactant aggregates in different micellar evolution. In each of the surfactant, there is overall catalysis with the catalytic factor  $(k_{obs} / k_w)$  ranging from 1 to 25.43. The rate of oxidation of brilliant green by carbonate ion increases with increase in chain length of the cationic surfactant which is an indication that the substrates are more reactive when micelles are formed from more hydrophobic surfactants. The rate constants increase in the following order:  $k_{DTAB} < k_{TTAB} < k_{CTAB}$  while the maximium catalytic factor is of the order: 8.16, 10.97, and 20.24 respectively.

In the  $k_{obs}$  – [Surfactant] profiles for CTAB, C<sub>16</sub>PyBr

and  $C_{16}$ TPPBr show also overall catalysis at all surfactant concentrations. The maximum factor is catalytic is 20.24, 25.43 and 4.28 respectively. These profiles are explained by change on the charge on head groups of the surfactants, the steric effect due to the donating effect of the electrons of the methyl and phenyl groups attached to the positive nitrogen atom in CTAB/C<sub>16</sub>TPPBr and stabilization of the positive charge on the nitrogen atom because of the resonance effect on pyridinium group of the head of the micelle in C<sub>16</sub>PyBr.

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# A DFT STUDY OF ADSORPTION OF ETHANE ON OXYGEN-COVERED PLATINUM CLUSTERS

Peter Kraus, Peter Lindstedt\* Department of Mechanical Engineering, Imperial College, Exhibition Road, London SW7 2AZ, UK

#### Abstract

The determination of accurate rates of adsorption of alkanes onto catalytic surfaces is a crucial step in the formulation of heterogeneous reaction mechanisms. The current study considers the case of adsorption on oxygencovered platinum clusters. Compared to ethane adsorption on clean platinum surfaces, the influence of oxygen coverage is not well understood, despite being particularly important under fuel lean conditions. The present work seeks to determine accurate adsorption and desorption rates for a reversible process using clusters featuring 10 and 20 platinum atoms. The potential energy surfaces are explored using the M06 family of density functionals along with the Stuttgart-Dresden effective core potential. The reaction rates are subsequently calculated using a multi-well technique (RRKM-ME) as implemented in MESMER. The impact of the determined rates are compared with a previously published mechanism derived using a reaction class based approach. It is shown that substantially improved agreement with experimental data is obtained under fuel lean conditions without any negative impact for fuel rich cases.

#### Keywords

Heterogeneous kinetics, DFT, Catalysis, Platinum, RRKM

#### Introduction

Ethane adsorption on pure platinum (Pt) surfaces has been investigated in some detail in the past (e.g. Zerkle et al., 2000; Kao et al., 2004; Vincent et al., 2008; Chen and Vlachos, 2010; Salciccioli et al., 2011; Raybaud et al., 2013). By contrast, oxygen-covered surfaces have not been extensively investigated. Zerkle et al. (2000) treat adsorption of ethane on a clean site as a two-step process leading to a surface reaction of  $C_2H_6(s_2)$  with O(s). Zheng et al. (2013) use the same pathway structure and identified the adsorption of ethane on oxygen-covered platinum surfaces as one of the most important reaction pathways under fuel lean conditions. Figure 1 shows a comparison of published experimental data (Zheng et al., 2013) for two fuel lean mixtures along with simulation results obtained using a collision-theory



Figure 1. Experimental data vs simulations

based mechanism (Vincent *et al.*, 2008) and an improved mechanism based on transition state theory (TST) (Kraus and Lindstedt, 2015). The major product ( $H_2O$ ) is well-predicted, especially by the improved mechanism. However, ethane conversion remains overpredicted along the reactor and following a sensitivity analysis, reaction (1) was identified as the most sensitive pathway

$$C_2H_6 + O(s) + Pt(s) \rightarrow C_2H_5(s) + OH(s)$$
(1)

The present work is accordingly focussed on investigating the adsorption and desorption rates on oxygen-covered platinum surfaces.

#### Method

The rate of the oxygen-mediated adsorption of ethane on platinum (*k*) has been estimated using a class-based approach of Vincent *et al.* (2008). The adsorption rate of ethane on the pure surface was scaled by the ratio of projected oxygen area  $(A_{O(s)})$  over the projected area of the metal atom  $(A_{Pt(s)})$ :

$$k \approx s_0 \frac{A_{0(s)}}{A_{Pt(s)}} \overline{v_{2D}} e^{\beta}$$
 (2)

In Eq. (2),  $s_0$  is the sticking coefficient of ethane on clean platinum,  $\overline{v_{2D}}$  the 2-dimensional Maxwellian velocity and  $e^{\beta}$  the Boltzmann factor. Recent

improvements involved utilising TST instead of collision theory (see Fig. 1). However, the scaling factor for the area shown in Eq. (2) was retained.



Figure 2. (a) – Class-based TST treatment, (b) – Idealised surface treatment.

The TST implementation uses DFT modelling of a simplified catalytic surface (Fig. 2a). A slab-based approach (cf. Fig. 2b) is preferable. However, DFT simulations of Pt surfaces featuring significantly more than 20 atoms are currently prohibitively expensive. The potential energy surface (PES) of ethane adsorption on platinum with pre-adsorbed oxygen was accordingly studied on two Pt clusters featuring 10 and 20 atoms starting from an ideal Pt(111) slab.



Figure 3. Potential energy diagram on Pt(10) cluster. Barriers in kJ/mol.

The computational methodology featured the M06-2X density functional (Zhao and Truhlar, 2008), following good results in the gas-phase study by Robinson and Lindstedt (2014). The DFT method was combined with the Stuttgart-Dresden effective core potential (Andrae *et al.*, 1990) for Pt atoms and 6-311G(d,p) for C, H and O atoms. All DFT simulations were performed using Gaussian 09 (Frisch *et al.*, 2009). The optimised reactants, intermediates, transition states and products were analysed using RRKM-ME as implemented in MESMER (Glowacki *et al.*, 2012) with rate parameters

fitted to the phenomenological rates via a Bartis-Widom analysis.



Figure 4. Optimised structures for Pt(20) case.

#### Results

The PES has two transition states (TS) as shown by the double daggers in Fig. 3. The first well, formed via TS ( $\ddagger^1$ ) and intermediate (I<sup>1</sup>), corresponds to dissociative adsorption of ethane, forming an ethyl group and surface hydrogen. The hydrogen radical then reacts with surface oxygen, following the path via TS  $\ddagger^2$  to products.

Table 1. Barrier heights in the forward direction.

Cluster	$1^{\text{st}}$ barrier $(\ddagger^1)$	$2^{nd}$ barrier ( $\ddagger^2$ )
size	[kJ/mol]	[kJ/mol]
Pt(10)	8.7	77.6
Pt(20)	6.3	51.1

The impact of increasing the cluster size from 10 to 20 Pt atoms is shown in Table 1. Both barriers decrease with cluster size, most likely due to stronger stabilisation of TS  $\ddagger^2$  by the Pt bulk. The barrier in the reverse direction also decreases with cluster size. As

shown in Fig. 5, the high-temperature reaction rates are relatively similar to the more simplistic estimation methods. However, the low temperature rate obtained using RRKM-ME is much slower.



Figure 5. Comparison of forward reaction rates.

By applying transition state theory to the Pt(10) system, ignoring the effects of the stabilisation of the intermediate, the low temperature rate becomes consistent with the simpler estimation methods, confirming that the effect of the second barrier is more important at temperatures below 1000 K.

Figure 6 shows a comparison of the RRKM rates based on the full vibrational structure to a set of rates where all Pt-Pt modes have been projected out, therefore only normal modes of C, H, O and two binding Pt atoms are considered here. As previously discussed, the low temperature rate on Pt(10) is mainly affected by the second barrier, with entropy effects only becoming



Figure 6. Effects of Pt-Pt vibrational modes.

important above 1000 K. On the contrary, the Pt(20) cluster calculation shows a large discrepancy, indicating a large entropy contribution.

Table 2. Pt(10) RRKM fitted Arrhenius parameters

А	β	E <sub>A</sub>
$[\text{kmol} / \text{m}^3\text{s}]$		[kJ / mol]
1.672784E+09	0.231	37.9

A three parameter Arrhenius fit to the Pt(10) RRKM series from Figs. 5 and 6 is presented in Table 2. The impact of the application of new rate determination is negligible under fuel rich conditions compared to the earlier estimations (Vincent *et al.*, 2008; Kraus and Lindstedt, 2015). However, under lean conditions (Zheng *et al.* 2013) the effect is profound. Four of the non-igniting lean cases are presented in Fig. 7. The agreement with experimental data is significantly improved, especially for the ethane conversion and at high-pressure.



Figure 7. Pt(10) RRKM rate (—) compared to the former TST-based (--) rate in non-igniting cases.

#### Conclusions

Adsorption of ethane on an oxygen-covered Pt surface has been studied using DFT on two Pt clusters. The PES is similar in shape for both clusters with two distinct wells. The increase in cluster size leads to a decrease in the second barrier from 77.6 to 51.1 kJ/mol with entropy contributions from the Pt-Pt vibrational modes significant in clusters above 10 Pt atoms. The RRKM reaction rates are arguably showing an erratic behaviour with changes in cluster size and the initial cluster structure is likely to be very important. A further investigation on a larger, embedded cluster, using ONIOM methods, is currently being carried out. Nevertheless, application of the rate obtained from the multi-well RRKM-ME investigation on the Pt(10) cluster leads to very encouraging results with substantial improvements in agreement with experimental data under fuel lean conditions with no negative impact on ethane-rich partial oxidation.

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# THE ART OF DEVELOPING A KINETIC MODEL DURING THE DESIGN OF AN INDUSTRIAL PACKED BED REACTOR: OXIDATIVE DEHYDROGENATION OF ETHANE TO ETHYLENE ON MoVTeNbO/TiO<sub>2</sub> CATALYST

Gamaliel Che-Galicia, R.S. Ruiz-Martínez, F. López-Isunza and C.O. Castillo-Araiza<sup>\*</sup> Grupo de Procesos de Transporte y Reacción en Sistemas Multifásicos, Depto. de IPH, Universidad Autónoma Metropolitana – Iztapalapa, Av. San Rafael Atlixco 186, 09340, México D.F., Mexico. \*To whom correspondence should be addressed: <u>coca@xanum.uam.mx</u>

#### Abstract

In this work we elucidate the importance of developing a suitable kinetic model to cope with the modeling of an industrial-scale wall-cooled packed-bed reactor. Specifically, statistical and phenomenological criteria at laboratory and industrial scale are used to select the most suitable model to describe the behavior of a highly active and selective catalyst (MoVTeNbO) for the ODH-Et. Firstly, three mechanisms based on different formalisms (Langmuir-Hinshelwood Hougen-Watson (LHHW), Mars-van Krevelen (MvK) and Eley-Rideal (ER)) are considered to develop the corresponding kinetic models, which, in turn, are evaluated via phenomenological and statistical criteria. All kinetics lead to parameter with physical and statistical reliability, thus, they are evaluated simulating the industrial-scale performance of a wall-cooled packed bed reactor for the said reaction-catalyst. A 2D pseudo-heterogeneous model that couples heat and mass transport phenomena to kinetics is used to. Mass transport parameters are obtained from literature, whereas, heat transport parameters are obtained from independent experiments in absence of reaction. The simulations are carried out at operating conditions relevant for industry: length and reactor diameter of 2.5 m and 2.5 cm, respectively; coolant temperature of 400-480°C; reaction mixture inlet temperature of 200°C, inlet molar concentration of 9/7/84 for C<sub>2</sub>H<sub>6</sub>/O<sub>2</sub>/N<sub>2</sub>; and particle Reynolds number of 1400. Results from laboratory and industrial scales lead to consider to the ER model as the most proper to be used to design the industrial-scale reactor since it is able to describe the sensitivity of the MoVTeNbO to produce carbon-oxides from ethane, a phenomenon that is not captured via LHHW and MvK.

#### Keywords

Oxidative dehydrogenation, Ethylene, MoVTeNbO catalyst, Reaction kinetics, wall-cooled packed bed reactor

#### Introduction

Ethylene is one of the most important olefins in the petrochemical industry since it is widely used as a feedstock to synthesize: polymers, styrene, ethylene oxide, vinyl chloride, vinyl acetate monomers, functionalized hydrocarbons (i.e., ethylene dichloride, ethylbenzene, acetaldehyde, and ethanol) and many other basic and intermediate chemical products. At the present time, ethylene is produced mostly by steam pyrolysis of diverse hydrocarbons streams and, in a minor grade, via fluid catalytic cracking (FCC) of gas oils and catalytic dehydrogenation of ethane (Weissermel and Arpe, 2003). However, these processes require relatively high temperatures and suffer from coking as well as uncontrollable side reactions. Thus, it is imperative to find competitive technologies to produce ethylene. In this regard, the oxidative dehydrogenation of ethane (ODH-Et) has, in principle, the advantages of low energy consumption, lower coke and CO<sub>x</sub> by-products, and high selectivity to ethylene compared to the conventional processes (Cavani et al., 2007). Notwithstanding there still advances for the successful application of the ODH-Et process at industrial level, the development of an effective catalytic system, able to selectively activate ethane toward ethylene at relatively low temperatures and at the same time minimize the unselective total oxidation routes to COx along with the proper design of the reactor technology are yet mandatory aspects to cope with.

So far, a broad variety of catalytic formulations to produce ethylene out of ethane in presence of oxygen have been investigated (Botella et al., 2004; López Nieto, 2002). From these formulations, the multimetallic mixed oxide catalyst based on Mo, V, Te and Nb is, undoubtedly, the most efficient and effective material since it presents an outstanding activity and selectivity to ethylene. However, there is still controversy on the macroscopic reaction mechanism for the ODH-Et. Aside, today there is no a defined industrial reactor technology for this reaction coupled to the fact that there is still controversy on the macroscopic reaction mechanism for the ODH-Et.

This work is aimed to investigate the importance of developing a proper kinetic model during the modeling of a reactor technology, i.e., industrial-scale wall-cooled packed-bed reactor for ODH-Et on a highly active and selective to ethylene catalyst (MoVTeNbO).

#### **Reaction kinetics**

As the reactor simulations concern the ODH-Et to produce ethylene on MoVTeNbO catalysts, various kinetic models have been recently developed. In order to investigate the influence of the kinetics on the industrial reactor behavior, three intrinsic kinetic models are considered: (i) the first model is based on a Langmuir-Hinshelwood-Hougen-Watson formalism (LHHW), (ii) the second model is supported on a Eley-Readel formalism (ER), while (iii) the third model is constructed on a Mars-van Krevelen formalism (MvK). Since physico-chemical parameters among the three different models are similar (i.e. activation energies, adsorption constants, etc.) and also present good statistically significant, a comparison between the kinetic models on the packed bed reactor performance is realized with the aim of elucidating criteria to select the most reliable kinetics to design the said reactioncatalyst at industrial scale.

The reaction network for ODH-Et over MoVTeNbO catalysts is proposed taking into account both parallel and consecutive reactions as follows:

Ethylene is produced from oxidative dehydrogenation of ethane  $(r_1)$ :

$$C_{2}H_{6} + 0.5O_{2} \rightarrow C_{2}H_{4} + H_{2}O$$
 (1)

Ethane can also be oxidized to form CO2  $(r_2)$  and/or CO  $(r_3)\text{:}$ 

$$C_{2}H_{6} + 3.5O_{2} \rightarrow 2CO_{2} + 3H_{2}O$$
 (2)  
 $C_{2}H_{6} + 2.5O_{2} \rightarrow 2CO + 3H_{2}O$  (3)

Ethylene can also react to form CO2 (r4) and/or CO (r5).

$$C_{2}H_{4} + 3O_{2} \rightarrow 2CO_{2} + 2H_{2}O \qquad (4)$$
$$C_{2}H_{4} + 2O_{2} \rightarrow 2CO + 2H_{2}O \qquad (5)$$

For the sake of brevity kinetic models are not presented here. Details about the kinetic models used in this work are given elsewhere [Che-Galicia et al., (2104; 2015)].

#### **Reactor Model**

The wall-cooled packed bed reactor model is based on averaged general conservation relations for

mass and energy but considering effective transport parameters. The 2D pseudo-heterogeneous model used is given as follows:

Gas phase:  

$$\epsilon \frac{\partial C_{n}}{\partial t} + u_{o} \frac{\partial C_{n}}{\partial z} = \epsilon D_{effr} \left( \frac{\partial^{2} C_{n}}{\partial r^{2}} + \frac{1}{r} \frac{\partial C_{n}}{\partial r} \right)$$

$$+ \epsilon D_{effz} \frac{\partial^{2} C_{n}}{\partial z^{2}} + (1 - \epsilon) k_{g} a_{s} (C_{ns} - C_{n})$$

$$\epsilon \rho_{f} C_{pf} \frac{\partial T}{\partial t} + u_{o} \rho_{f} C_{pf} \frac{\partial T}{\partial z} = k_{effr} \left( \frac{\partial^{2} T}{\partial r^{2}} + \frac{1}{r} \frac{\partial T}{\partial r} \right)$$

$$+ k_{effz} \frac{\partial^{2} T}{\partial z^{2}} + (1 - \epsilon) h_{g} a_{s} (T_{s} - T)$$
(6)
(7)

Solid phase:

$$(1-\varepsilon)\frac{\partial C_{ns}}{\partial t} = (1-\varepsilon)k_{g}a_{s}(C_{n}-C_{ns}) + \rho_{b}\sum_{i=1}^{5}\nu_{ni}r_{i}$$
(8)

$$\rho_{b}C_{ps}\frac{\partial T_{s}}{\partial t} = (1-\varepsilon)h_{g}a_{s}(T-T_{s}) + \rho_{b}\sum_{i=1}^{5}(-\Delta H_{i})r_{i}$$
(9)

The corresponding initial and boundary conditions are:

$$t = 0; \quad C_{n} = C_{n,ss} \text{ and } C_{ns} = C_{ns,ss}$$
 (10)

$$T = T_{ss}$$
 and  $T_s = T_{s,ss}$  (11)

$$z = 0; \quad u_{o}C_{no} = u_{o}C_{n} - \varepsilon D_{effz} \frac{\partial C_{n}}{\partial z}$$
 (12)

$$u_{o}\rho_{f}C_{pf}T_{o} = u_{o}\rho_{f}C_{pf}T - k_{effz}\frac{\partial T}{\partial z}$$
(13)

$$z = L; \quad \frac{\partial C_n}{\partial z} = 0 \text{ and } \quad \frac{\partial T}{\partial z} = 0$$
 (14)

$$r = 0;$$
  $\frac{\partial C_n}{\partial r} = 0$  and  $\frac{\partial T}{\partial r} = 0$  (15)

$$r = R_{t}; \quad \frac{\partial C_{n}}{\partial r} = 0 \text{ and } k_{effr} \frac{\partial T}{\partial r} = h_{w}(T - T_{b})$$
 (16)

where  $C_n$  is the molar concentration of component n in the gas phase,  $D_{effr}$  is the radial mass dispersion coefficient,  $D_{effz}$  is the axial mass dispersion coefficient,  $\rho_b$  is the fixed-bed density (active catalyst density),  $\rho_f$  is the fluid density,  $C_{pf}$  is the specific heat capacity of the fluid,  $C_{ps}$  is the specific heat capacity of the solid,  $k_{effr}$  is the radial effective thermal conductivity,  $k_{effz}$  is the axial effective thermal conductivity and  $h_w$  is the wall heat transfer coefficient. This reactor model accounts for the role of hydrodynamics through the proper estimation of heat transport parameters (i.e.,  $k_{eff}$  and  $h_w$ ) in absence of reaction (Castillo-Araiza et al., 2007). The performance of the reactor is evaluated by the conversion of reactants as well as by the yield of products.

The resulting model is given in terms of a set of parabolic partial differential equations, which is solved numerically by the method of orthogonal collocation using 5 and 50 interior collocation points at the radial and axial coordinates, respectively, employing shifted Legendre polynomials. The resulting set of ordinary differential equations is, then, solved by a Runge-Kutta method.

#### Results

The reactor simulations are carried out at the following conditions that are relevant for industry: length and reactor diameter of 2.5 m and 2.5 cm, respectively; coolant temperature of 400-480°C; reaction mixture inlet temperature of 200 °C, inlet molar concentration of 9/7/84 for  $C_2H_6/O_2/N_2$ ; and particle Reynolds number of 1400 with a tube to particle diameter ratio equal to 3.12. Kinetic results, not shown here for brevities sake, indicate that the three kinetic models describe adequately experimental data obtaining parameters statistically significant and physically meaningful (i.e., F value for LHHW is 7567, for ER is 7642 and for MvK is 2038).



Figure 1. Temperature profiles using different kinetic models with: inlet molar ratio  $C_2H_6/O_2/N_2=9/7/84$ :  $T_b$  of 440 °C.

Predictions at  $T_b$  of 440 °C lead to ethane conversions of 12.36% (LHHW), 20.28% (ER) and 6.77% (MvK) and ethylene yields of 11.58% (LHHW), 19.05% (ER) and 6.4% (MvK). Regarding temperature, ER approach predicts the presence of a mild hot spot (ca. 7 °C), vide Fig. 1, that is not observed when using the LHHW and MvK models. From these results, we can infer that even thought the models are statistically accepted by standard literature, the proper evaluation of the kinetic phenomenon along to the statistical tests is mandatory for suitable predictions at industrial reactor level. Thus, the MvK kinetic model is the less reliable kinetic model due to the smallest global statistical

significance (F value=2038). Otherwise, albeit LHHW and ER kinetic models present similar global statistical significance there are important differences in predictions at industrial reactor performance, Therefore, a final criterion has to be taken into account to discriminate among the ER and LHHW kinetic models in order to have the best candidate to be used in the conceptual design of ODH-Et reactor in future investigations. In this respect, a comparison between these two kinetic models is realized based on the Bayesian information criterion (BIC) (Schwarz, 1978), which not only takes into account the difference in the residual sum of squares between competing models, but also accounts for a possible difference in number of parameters. Applying the criterion that the model with the minimum value of BIC is the most suitable model, the ER model presents the lowest value of BIC compare to the LHHW model, having an absolute difference ( $\Delta$ BIC) of ca. 50. Furthermore, observations stated by Che-Galicia et al., (2014) showed how the ethane feed concentration has a positive effect on ethane conversion. For instance, augmenting the ethane feed concentration from 6 mole % to 28 mole % lead to an important increase in the ethane conversion. In this regard, MvK and LHHW kinetics are not able to describe laboratory observations related to the role of inlet concentration of ethane on conversion (not shown), whereas the ER formalism captures such phenomenon. From this end, LHHW model makes an overfitting, i.e., ethane adsorption term leads to results but to inadequate adequate statistical observation descriptions. For instance, ethane fractional coverage along the reactor varied from 7.5% to 51.6%, 49.8% to 90.6% and 69% to 95% for 1% mole, 9% mole and 18% mole of ethane at the reactor inlet, respectively. Therefore, LHHW kinetics predicts ethane adsorption rather than its total oxidations as does ER kinetics.

The performance of MoVTeNbO system during the ODH-Et in an industrial scale wall-cooled packed bed reactor is evaluated through the variation of coolant temperature (400 - 480 °C) using the ER kinetic model. Fig. 2 displays temperature, conversion (ethane and oxygen) and yield (ethylene, CO<sub>X</sub> and water) profiles along the reactor length at different coolant temperatures maintaining a fixed inlet molar ratio C<sub>2</sub>H<sub>6</sub>/O<sub>2</sub>/Inert=9/7/84. So far, an increment in coolant temperature causes an increment on the magnitude of the hot spot, vide Fig. 2a. Specifically a  $T_b$  of 400 °C or 440 °C leads to a mild hot spots of ca. 1 °C and 7 °C respectively whereas a T<sub>b</sub> equal to 480 °C provokes a pronounced hot spot with a temperature rise of ca. 56 °C. In the latter, the rate of heat removal is minor in comparison with the rate of heat generated. Besides Figs. 2b-d displays the effect of coolant temperature on the overall consumption rates of the reactants. The increment of T<sub>b</sub> favors both ethane and oxygen conversions. Analyzing the product distribution, an increase in T<sub>b</sub> brings out a positive effect on the yield of ethylene out of ethane. However, a higher  $T_b$  leads to higher carbon oxides yields, which are the responsible of both the formation of hot spots and the decrease in the selectivity to ethylene. In this regard, a lower  $T_b$  is recommended for a satisfactory ethane conversion along with ethylene selectivity avoiding catalyst damage due to high temperatures (Valente et al., 2014). The behavior of the industrial scale reactor presented in Fig. 2 shows similar tendencies as those of the typical industrial-scale packed bed reactors used to perform highly exothermic reactions (Castillo-Araiza and López Isunaza, 2010; 2011).



Figure 2. Reactor model predictions at different  $T_b$  with an inlet molar ratio  $C_2H_6/O_2/N_2=9/7/84$ : (a) Temperature profiles; (b) Conversion and yield profiles at  $T_b=440$  °C; (c) Conversion and yield profiles at  $T_b=440$  °C; (d) Conversion and yield profiles at  $T_b=440$  °C; (d) Conversion and yield profiles at  $T_b=480$  °C (For (b)-(d): ( $\bullet$ )  $C_2H_6$  conversion; ( $\Box$ )  $O_2$  conversion; ( $\circ$ )  $C_2H_4$  yield; ( $\blacksquare$ )  $H_2O$  yield; ( $\blacktriangle$ ) CO yield and ( $\triangle$ ) CO yield.

In the design of this type of complex reactors it is necessary to operate without the presence of drastic hot spots in order to decrease the irreversible deactivation of the catalysts by a sintering phenomenon. Particularly, the stability of the MoVTeNbO catalyst is restricted to operate below ca. 500 °C, due to energy saving but, mainly, because operations above 500 °C leads to the irreversible loss of catalytic activity as a consequence of the removal of tellurium from the MoVTeNbO catalytic formulation (Valente et al., specifically, the lost of Te from 2014), i.e. MoVTeNbO material occurs preferentially from the end section of the M1 crystal phase, across the [001] plane. The removal of Te species modifies the crystal phase composition of the M1 phase causing the partial destruction of the MoVTeNbO with the simultaneous formation of the MoO<sub>2</sub> phase and, in consequence, the activity and selectivity to ethylene are affected as elucidated elsewhere (Valente et al., 2014).

#### Conclusions

The kinetic model selection is a key point to obtain a successful prediction of an industrial reactor. Kinetic models developed in this research leaded to different prediction of the modeled industrial-scale packed-bed reactor. These differences are not only caused by the disparity of the statistical significance of each model, but also are caused by phenomenological aspects, i.e. the adsorption of reagents and products. In this regard, laboratory and industrial modeling criteria elucidate that the ER formalisms is the most proper one to develop the kinetic model for the ODH-Et on a MoVTeNbO catalyst.

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### **Co-Processing of Waste Plastic and Hydrocarbons over HZSM-5**

N. Carmo<sup>a</sup>, D. Afonso<sup>a</sup>, E. Santos<sup>a</sup>, I. Fonseca<sup>b</sup>, F. Lemos<sup>a</sup>, M.A.N.D.A. Lemos<sup>a\*</sup>

<sup>a</sup>CERENA, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

<sup>b</sup>REQUIMTE-CQF – Universidade Nova de Lisboa, Faculdade de Ciências e Tecnologia, Campus da Caparica, 2829

Caparica, Portugal

#### Abstract

High and low density polyethylene (HDPE and LDPE, respectively) and waste plastic film (polyethylene based plastic wastes) thermal and catalytic degradation were analysed through simultaneous thermogravimetry (TG) and differential scanning calorimetry (DSC) in inert atmosphere. Catalytic degradation of the plastic film was performed using HZSM-5 zeolites. Although the catalyst induces a large decrease of the degradation temperature for polyethylene there is little effect of the catalyst on the waste plastic degradation temperature. Mixtures of waste plastic with (nC50) paraffin were also analysed. The results show that the presence of the hydrocarbon in the mixture grants some protection to the catalyst, allowing it to retain part of its activity during the process even in the presence of the waste contaminants. These findings suggest that larger hydrocarbon: waste plastic ratios promote higher protection to deactivation and that waste plastic co-processing with oil is feasible.

#### Keywords

Polyethylene, waste plastic, pyrolysis, catalytic cracking.

#### Introduction

Plastic materials have a profound contribution towards the advancement of the quality of life and, due to continuing evolution in technologies and to new scientific achievements, are used extensively in daily life as well as in industries, playing the role of an indispensable ingredient due to their versatility and low cost. The increased use of different types of plastics has also increased the amount of waste released into the environment. Serious environmental problems are caused by these waste plastics because of their low density and large volume (Cho et al., 2010; Zhang et al., 2015).

There are several possible routes for plastic waste management. In Europe plastic waste management is distributed between 53% land filling, 29% incineration, 16% mechanical recycling and 2% feedstock recycling (Obeid et al., 2014), landfill and incineration are still widely used for the disposal of plastic waste, but the deposition of these plastic waste in landfills, cause serious danger to the environment, due to plastic degradation and subsequent generation of contaminants to the soil (Miguel et al., 2009; Lopez et al., 2011) and constitute a significant waste of a valuable material.

Feedstock recycling, converting waste plastic into useful chemicals, is a relevant alternative and, in particular, pyrolysis is a well-established process that can be used to convert plastics to more valuable chemicals and fuels. As for catalytic pyrolysis, a suitable catalyst is used to drive the cracking reaction and the presence of this catalyst reduces the temperature and reaction time, providing also a product distribution more favourable for the production of liquid fuels (Ahmad et al., 2013). mandal@tecnico.ulisboa.pt

In the present work we aim to study the catalytic pyrolysis of a waste plastic, mainly containing polyethylene, for the production of fuels. Since this process is quite similar to catalytic cracking we will also analyze the influence of the presence of a hydrocarbon, like n-triacontane (n-C30), n-tetracontane (n-C40) and n-pentacontane hydrocarbon (n-C50) in a perspective of co-processing waste with oil.

#### **Experimental**

#### Plastic polymer and catalyst

Three plastic samples were used in this work: the pure unadditivated polyethylene samples, kindly supplied by Repsol, consisting of a high density polyethylene (HDPE) in powder form, with melt flow indexes MFI5 = 0.39 g/10 min, MFI21 = 11.8 g/10min, MFI21/MFI5 = 30 and a molecular weightMw~290,000 (Mw/Mn~20) and low density polyethylene (LDPE) samples showing a molecular weight, Mw (LDPE) 376,000 (Mw/Mn~23); the other one was an actual PE rich waste fraction, collected and separated from municipal waste (WP).

The hydrocarbons used in this work are long chain alkanes such as:

n-triacontane  $(n-C_{30})$  – molar mass 422.81g/mol, purity 99% and supplier Fluka.

n-tetracontane  $(n-C_{40})$  – molar mass 563.08g/mol, purity 98.5% and supplier Fluka.

n-pentacontane  $(n-C_{50})$  – molar mass 703.34g/mol, purity 97% and supplier Aldrich.

The catalyst used was HZSM-5 commercially supplied by Zeolyst, with a molar Si/Al ratio equal to

15; the catalyst was calcined before use at 500  $^{\circ}$  C for 8 hours in 0.5  $L_{dry air.}g^{-1}_{zeolite.}h^{-1}$ .

#### Thermogravimetric analyses

All DSC/TG experiments were carried out in a TA Instruments SDT 2960 simultaneous DSC-TGA apparatus. Prior to the experiments, the TG-DSC apparatus was calibrated according to the manufacturer's specifications, in relation to weight, temperature and DSC signals.

The test starts by equilibrating the sample at 40 °C for 10 min; the sample is then heated from 40 °C up to 600 °C at 10°C/min. The sample was then kept at 600 °C for 10 minutes and cooled down to room temperature. Unless otherwise specified all the experiments were carried-out under a continuous flow of nitrogen of 80 ml/min.

#### **Results and discussion**

The results collected in this study were compared to the thermal degradation of pure HDPE and LDPE. Results for the degradation of the pure plastics are depicted in Figures 1 and 2.



Figure 1. Heat flow and mass loss curves for pure HDPE (see text for conditions).



Figure 2. Heat flow and mass loss curves for pure LDPE (see text for conditions).

Two peaks are observed, the first corresponding to the melting of the plastic, and the second peak corresponding to the degradation of the analyzed material.

The mass loss associated with the degradation occurs due to successive breakage of the bonds in the compound that leads to the production of increasingly smaller compounds, which will eventually be volatile at the reaction temperature and evaporate, leading to the weight loss that is observed (Coelho et al., 2010).

Let us focus on at this point in the study of the waste plastic (WP). In Figure 3 we show the results of DSC-TGA for this waste plastic.



Figure 3. Heat flow and mass loss curve for the thermal degradation of WP (see text for conditions).

Figure 3 shows the behavior of the waste plastic; the overall behaviour is similar to that previously recorded in the pure plastics: a melting peak, consistent with the composition being mainly polyethylene (see Table 1) and the degradation peaks; in the case of waste plastic there are more than one peak in the degradation area, probably due to the fact that the waste plastic is a mixture of wastes containing predominantly polyethylene, but of different origin and also other components, including organic contaminants.

In the temperature range corresponding to the degradation peaks, we have two relevant mass losses which can be seen in Figure 3. The first one, at lower temperature, is associated with the first variation observed in the heat flow curve, and appears to be poorly defined, while the second mass loss corresponds to a much more defined endothermal DSC peak. The latter should correspond to the moment where the major degradation occurs and the heat flow curve is much similar to the one observed for the pure polymers. However, while in pure polymers an almost complete mass loss occurred after the degradation, in this case the initial mass is not completely degraded, and some impurities remain at the end of the test, possible associated with inorganic contaminants, including fillers used in commercial plastics.

Table 1 shows the values of the peaks associated with melting and degradation of samples of HDPE, LDPE and waste plastic (WP).

Table 1. Melting and thermal degradation temperatures for various polymers at a heating rate of

Samples	Peak melting temperature (°C)	Peak degradation temperature
HDPE	137.4	485.1
LDPE	118.8	472.4

|--|

As can be seen from Table 1 both the melting and the degradation temperatures for waste plastic are very similar to the values of high density polyethylene, confirming that this is, in fact, the major component in the sample. These values are agreement with data from the literature (Aboulkas et al., 2007).

In order to test the effect of the catalyst on waste plastic, a similar test was made but adding 1 mg of catalyst to the sample in the pan. The results are shown in Figure 4.



Figure 4. Heat flow and mass loss curves for WP + catalyst (see text for conditions).

We can see in Figure 4 that the behaviour is similar to what happens without catalyst. It is also noteworthy that, while the presence of the catalyst decreases significantly the degradation temperature for pure HDPE, as observed in previous works (Coelho et al., 2012), the decrease in the peak temperature in this case is only approximately 10°C. This fact is probably due to the presence of various contaminants in the sample that are likely to deactivate the catalysts.

For the work in question, we also wanted to check if these preliminary results would hinder the use of catalysts to degrade waste plastic. However, it is also true that in an oil refinery some of the components that are present in the feed of an FCC unit, which operates under similar conditions to the ones that are required for the waste plastic processing, also deactivate the catalyst.

To analyse the possibility of co-processing waste plastic with oil, we investigated the effect of mixing the waste plastic with hydrocarbons on the overall outcome, since, at the industrial level, the goal would be to treat the waste plastic mixed with feedstock for the cracking process in the refinery (Lee, 2008).

In the following sequence of tests we investigated the behaviour of a mixture of WP and a long-chain hydrocarbon in the presence of the catalyst, varying both the hydrocarbon used,  $C_{30}$ ,  $C_{40}$  and  $C_{50}$ , and the WP/hydrocarbon ratio. A sample of the results is depicted in Figures 5. For these experiments, the ratio WP/hydrocarbons is (1:1/2) and the mass of catalyst is 1mg.





From the heat flow curves we can see that there are two melting peaks, one corresponding to the plastic and the other one to the hydrocarbon, as well as two degradation peaks. (See also Table 2).

Table 2. Melting and catalytic degradation temperatures for the mixtures of waste plastic and hydrocarbons

Samples	Peak n tempe (•	nelting rature C)	Peak deg tempe (•	gradation rature C)
WP + C <sub>30</sub> (1:1/2)	77.0	129.2	380.1	480.6
WP + C <sub>40</sub> (1:1/2)	90.8	131.2	394.5	482.0
WP + C <sub>50</sub> (1:1/2)	103.2	131.4	390.1	482.5

As it can be seen, no significant difference in the WP degradation temperatures were observed after the introduction of the hydrocarbon. However, in this first attempt the proportion of WP to hydrocarbon favoured the WP and, in a real case scenario, this would probably not be the case and the oil feed would probably outweigh the waste plastic one. Thus, we have tested the presence of the hydrocarbon (C50) with different ratios of hydrocarbon and plastic film.

In the following experiments the amount of catalyst added was always approximately 1 mg and the total amount of degradable material (waste plastic + hydrocarbon) was also kept constant. We analysed several WP/hydrocarbon ratios of (1:2) (1:3) (1:6) (1:12) and the Heat Flow signals for the lower and the higher ratios are depicted in (Figure 6).



Figure 6. Comparison of the heat flow curves for the catalytic degradation of the waste plastic and C50 mixture, for two different WP/C50 ratios.

The data on melting and degradation temperatures for the different WP/C50 ratios is presented in Table 3.

Table 3. Melting and degradation temperatures for the
catalytic degradation of the plastic film and C50
mixture, with varying ratios between the two
components

Samples	Peak melting temperature (°C)	Peak degradation temperature (°C)	
WP + C <sub>50</sub> (1:2)	105.1	373.7	433.5
WP + C <sub>50</sub> (1:3)	102.9	347.0	430.7
WP + C <sub>50</sub> (1:6)	101.7	323.5	454
WP + C <sub>50</sub> (1:12)	100.0	321.6	441.4

We can see from the data in Figure 6 and Table 3 the increase in C50 in the mixture makes the melting temperature increasingly closer to that of the hydrocarbon, although it is likely that the melting peak corresponding to HDPE is concealed by the large signal from the melting of the hydrocarbon. Additionally we can still see two separate degradation peaks but the protection effect on the catalyst is quite clear – not only the catalytic degradation of C50 approaches that of the pure component but also the degradation temperature for the plastic component has decreased by amounts ranging from 30 °C to 50°C.

#### Conclusions

From the results presented here we can conclude that the contaminants found in the samples of waste plastic in this study can be quite deleterious for the acidic catalyst used to accelerate the plastic degradation.

Since it is expected that feedstock recycling will be most important in highly contaminated plastics that can not be subject to mechanical recycling, this is an aspect to be taken into consideration. However, the co-processing of plastic waste with hydrocarbons suggests that it is possible to cofeed plastic waste into a conventional FCC unit, as long as the proportion of plastic waste to hydrocarbon feed remains limited.

Further studies will still be required so as to ascertain how this may impact on the lifetime expectancy of the FCC catalyst.

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#### STABILITY OF HUMATE AGGREGATES IN PRESENCE OF PESTICIDES

J. Morales<sup>a,\*</sup>, A Cid<sup>b</sup>, O. Moldes<sup>a</sup> and J.C. Mejuto<sup>a</sup>

a) Department of Physical Chemistry, Faculty of Sciences, University of Vigo, 32004 Ourense, (Spain)

b) Chemistry Department, REQUIMTE-CQFB, New University of Lisbon, 2829-51-6 Monte da Caparica, (Portugal)

#### Abstract

A study of the surface charge of humic acids aggregates has been investigated to focus on those physical properties (Zeta potential, the particle diameter, the polydispersity, the conductivity and mobility) that have a high impact on their chemical reactivity in absence and in the presence of pesticides. For this purpose, it has been considered the effect of pH and ionic strength on these properties. Making the use of specific properties of humic substances colloidal aggregates, and more specifically one type of humic substances, the humic acids (HAs). A destabilization effect on the system has been observed when we included pesticides in these media, with greater effect for carbofuran than for metalaxyl.

#### Keywords

Colloids, stability, humic acid, surface charge, Zeta potential, carbufuran, metalaxyl

#### Introduction

Organic matter in soil, and more specifically humic substances (Davies et al. 1998), facilitates the adsorption mechanisms of hazardous substances such as pesticides (Kinniburgh et al., 1996; Zhou et al., 2005; Li et al., 2003). They also increase the degradation and, decrease the volatilization of the xenobiotics (Briceño et al., 2007). The long-time effect of these xenobiotics is an important point of Green Chemistry and Environmental Chemistry. We must take into account that some pesticides remain active for years, but others are degraded only in few days. So, the different degradation mechanisms are very important (microbiologic activity, photolysis and other chemical process). For this purpose, two pesticide have been selected, carbofuran (CF) and metalaxyl (M). The first one, it is extensively used in agriculture as a systemic insecticide in order to control nematodes, rootworms and beetles on corn, rice and potatoes (Ballantyne et al., 1993). The second one, it is a phenylamide fungicide sprayed to control downy mildew and oömycetes (Wilson et al., 2001). From a chemical point of view, the study of the catalytic role of HAs as colloidal aggregates on decomposition processes of various pesticides gains interest. Recent studies showed that the presence of micellar aggregates (Astray et al., 2011; Morales et al., 2012) can significantly change the kinetic processes of degradation of some of these xenobiotics, being especially important the role of the HAs in various processes of environmental interest (Astray et al., 2010; Morales et al., 2013A; Morales et al., 2015). The aim of this work is to analyse if the presence of pesticides could decrease the stability of these natural aggregates.

32004 Vigo, Ourense, (Spain). Email: xmejuto@uvigo.es **Experimental Procedure** 

The two pesticides analysed in the present work (Figure 1), carbofuran and metalaxyl, were obtained from Sigma-Aldrich. Other reagents (sodium hydroxide, nitric acid, methanol and acetonitrile) were supplied by Panreac. Humic acids used in this study were isolated using the method described elsewhere (Sparks, 2009). All aqueous solutions were prepared by weight using double-distilled water.



#### Figure 1. Structural formula of CF and M.

Zeta potential  $(\zeta)$ , polydispersity (Đ). conductivity ( $\kappa$ ), mobility ( $\mu$ ) and the particle size ( $R_h$ ) determination were measured using a Malvern Zetasizer by DLS. Detailed experimental procedure has been described elsewhere (Morales et al., 2013B). All experiments were measured at 25 °C.

#### **Results and Discussion**

To whom all correspondence should be addressed: Department of Physical Chemistry, University of

Zeta potential ( $\zeta$ ) is a physical-chemical parameter to describe electrostatic interactions and ion adsorption between charged particles (Leroy et al., 2011). The excess of electrical charge at the interface is responsible for surface conductance and, it is known that, is a good parameter to evaluate the stability of colloids. It has been determined that there is a correlation between some physical and chemical characteristics of colloidal aggregates from extracts of soil's HAs as pH changes,  $\kappa$  and, especially,  $\zeta$ .

When all particles in suspension have a high negative or positive  $\zeta$  then they will tend to repel each other and, consequently, there will not have tendency to flocculate. However, if these particles have low  $\zeta$  values, there is no force to prevent the particles coming together and flocculating. General division line between stable and unstable suspensions is generally taken at either +30 mV or -30 mV. So, particles with  $\zeta$  more positive than +30 mV or more negative than -30 mV are normally considered stable (Vanysek, 2009). According to the literature (Evans et al., 1999), we could consider we are working in a natural colloidal aggregate media formed by humic substances dispersions in water.



Figure 2. Influence of [HAs] and pH on the Zeta potential in absence of pesticide.

The stability of HAs aggregates is strongly influenced by the pH. In fact, on increasing the pH value and the HAs contain of the dispersion, the stability of micellar aggregates increases. According to the experimental data obtained, only at HAs concentration lower than 5.00 x  $10^{-3}$  g·L<sup>-1</sup>,  $\zeta$  values greater than -30 mV were found, which means instability of colloids (Figure 2). In the range of pH=6.5 and pH=12 and for concentration of HAs greater than 5.00 x  $10^{-3}$  g/L,  $\zeta$  value is always lower than -30 mV. These values decrease when we increase pH and HAs concentration, around -60 mV for colloids which contain HAs concentration=0.8 g·L<sup>-1</sup>.

Figure 3 shows the influence of HAs concentration at pH constant (as an example at pH=9 and in presence of CF). The observed effect is due to the increase of the surface charge related with

deprotonation of phenolic and carboxylic groups presents in HAs. These groups will be equivalent to the polar head-group in the "traditional" surfactants (Mouvenchery et al., 2012). The presence of CF implies a decrease in the colloids stability. This decrease is higher when the HAs concentration decreases. At low HAs concentration, [HAs]=0.02 g·L<sup>-</sup> <sup>1</sup> and pH=6.7, the  $\zeta$  value in the presence of CF implies an increase of 20% (-44.8 mV in the absence and -36.2 mV in the presence of CF, respectively). Similar values has been found when pH values were increased. Then, at pH=8.5 the stability decreases approximately around to 15% and, at more basic pH values it decreases between 18 and 20%, respectively. The presence of CF low HAs concentrations could imply floculation/coagulation process because  $\zeta$  values are near 30 mV. Although these processes will be related not only to the presence of carbofuran but also to the presence of its hydrolysis products (Arias et al., 2005). Different variation upon the stability of the natural colloidal aggregates in the presence of CF has been observed when HAs concentration increased. For example, at [HAs]=0.4 g·L<sup>-1</sup> and at pH=7.8,  $\zeta$  value shows a decrease from -50.0 mV to -45.4 mV, around 9.2 % of destabilization of the media. Hovewer, at [HAs]=0.6 g·L<sup>-1</sup> and at pH=7.4,  $\zeta$  value shows a decrease around 2%, from -53.1 mV to -52.4 mV. Figure 3 shows a clear trend in which the increase of the concentration of HAs. The OH<sup>-</sup> presence causes the basic hydrolysis of CF and, consequently, this hydrolysis is inhibited by the presence of HAs. It implies that the most destabilizing factor of these natural colloidal aggregates composed by HAs was associated not directly by the presence of pesticide but to the hydrolysis products thereof. Since with the increase of HAs concentration, the hydrolysis process and therefore slows down the conversion rate of CF in its degradation products.



Figure 3. Influence of [HAs] on  $\zeta$  in the presence of carbofuran at pH=9.

The presence of M implies a decrease in the colloids stability too. This decrease is increased when

HAs concentration decreases in the colloid. In fact, at pH=6.8 values and HAs concentration of 0.02 g·L<sup>-1</sup>, the presence of M implies that  $\zeta$  decreases from -44.8 mV to -39.9 mV, which represents a 10% decrease of aggregate stability. This behaviour was observed in all pH range studied, and it has been observed a decrease of 12 % at pH=9.3 ( $\zeta$ =44.8 mV to  $\zeta$ =-39.3 mV) and around 17% at pH=11.9 ( $\zeta$ =42.7 mV to  $\zeta$ =-35.4 mV). Whereas, in all cases studied the influence of M is lower than CF. Even when CF levels were near to values that could cause problems of flocculation/coagulation of the system.



Figure 4. Influence of HAs concentration on the  $\zeta$  in the presence of metalaxyl at pH=9.

Increasing the HAs concentration, it has been appreciated variations on the effect in the media by the presence of M. At high HAs concentrations, the observed behaviour (around 3-6% of destabilization) implies a system destabilization significantly lower than at [HAs]=0.02 g·L<sup>-1</sup>. For example, at [HAs]=0.2  $g \cdot L^{-1}$  and pH=6.5, the  $\zeta$  value varied from -46 mV (in absence of pesticide) to 44.5 mV (in the presence of M). It was observed a slight increase in the destabilization around 5% (from -46.4 mV to -44.1 mV) when the pH was increased. At basic pH lower values (at pH=11.9, -46.5 mV in absence and -44.9 mV in the presence of M, respectively) the destabilization remained around of 4%. Figure 4 shows the  $\zeta$  variation and the influence of HAs colloidal aggregates in the presence of M at pH=9.

To sum up, the pesticide addition causes a desestabilization of the HAs colloidal aggregates in solution, thus modifying some of its properties associated with its colloidal nature. The inclusion of CF shows greater destabilization effects on the system than the M inclusion (Figure 5). This behaviour can be explained in terms of the hydrophobicity of the different xenobiotics. The value of logP for CF and M are 2.32 and 1.65, respectively (Hansch et al., 1995). The greatest value for CF implies that the interaction between the agricultural xenobiotic and HAs is stronger than the corresponding one between M and the

natural aggregate colloid. Consequently, CF penetrates deeply inside the micelle considering that the main driving force of the association of these hummate aggregates is hydrophobic/hydrophilic force. For these two reasons, we could assume that the structural distortion of micelle is more important in the presence of CF. This fact would justify the stronger effect upon micellar aggregate stability observed.



Figure 5. Variation of  $\zeta$  and influence of the pesticide in the HAs colloidal aggregates. [HAs]=0.02 g·L<sup>-1</sup>: in absence of pesticide ( $\bullet$ ), in the presence of CF ( $\blacksquare$ ) and in the presence of M ( $\nabla$ ).

Finally, the study of other physical and chemical parameters (the particle size, the conductivity, the polydispersity and the mobility) to characterize these hummate colloidal aggregates has been investigated, both in the absence and in the presence of CF and M, within no significant changes associated to the pesticide inclusion in these natural colloidal aggregates media. As an example, Table 1 shows some of these chemical parameters in the presence of CF at  $[HAs]=0.4 \text{ g}\cdot\text{L}^{-1}$ .

Table 1. Physical and chemical parameters of HAs in the presence of CF.  $[HAs]=0.4 \text{ g} \cdot L^{-1}$ ;  $[NaOH]_1=0.25$ M;  $[NaOH]_2=0.025 \text{ M}$ ;  $[HNO_3]=0.25 \text{ M}$ .

			_
pH	µ / □·cm·Vs	R <sub>h</sub> / nm	Ð
7.51	-3.77	305.7	0.585
7.90	-3.79	296.3	0.558
8.33	-3.87	298.3	0.588
8.76	-3.59	320.3	0.584
9.27	-3.69	305.2	0.568
9.86	-3.49	300.2	0.549
10.40	-3.59	290.6	0.567
10.90	-3.75	294.7	0.563
11.30	-3.78	279.2	0.569
11.90	-3.70	286.8	0.619

#### Conclusions
The colloidal behaviour of the AHs in the presence of pesticides can be significantly influenced by the solution pH. In fact, modification in the  $\zeta$  have been observed. The presence of pesticides (both M and CF) in the analysed media decreases the stability of like-micelles natural aggregates. In fact, these effects are more pronounced at lower HAs concentrations. Moreover, the inclusion of CF has a greater effect on the system than the M inclusion. This behaviour is due to the hydrophobicity of the different xenobiotics analysed in the present work.

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# KINETICS OF PHENOL HYDRODEOXYGENATION OVER A NiMo/γ-Al<sub>2</sub>O<sub>3</sub> CATALYST

Papastylianou A., Templis Ch., Papayannakos N.\* Department of Chemical Engineering, National Technical University of Athens, 9, HeroonPolytechniou Str., Gr-15780 Zografos, Athens, Greece.

## Abstract

A kinetic study of the catalytic hydrodeoxygenation of phenol in liquid-phase over a commercial NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst in crushed form was performed using results from experiments conducted at pressures 20 – 40 bar and temperatures 130 – 170 °C. The detected products were phenol, cyclohexanol, cyclohexane, cyclohexene and traces of benzene. The experimental results indicate that cyclohexane yield increases with temperature and decreases with pressure and WHSV increase. Benzene and cyclohexanol hydrotreatment experiments have also been carried out to reveal the reaction paths followed for the phenol hydrodeoxygenation over the NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. All experimental data were used to develop a kinetic model for the phenol conversion.

# Keywords

Hydrodeoxygenation, phenol, NiMo/y-Al<sub>2</sub>O<sub>3</sub>

#### Introduction

Cellulosic biomass can be converted into transportation fuels bythree major pathways: syngas production by gasification, bio-oil production by pyrolysis or liquefaction and aqueous sugar production byhydrolysis. Bio-oilis considered as an alternativeto petroleum-based sources for a wide range of fuels and high value-added chemicals and other products. The major organiccompounds of the bio-oils are acids, alcohols, ethers, ketones, aldehydes, phenols, esters, sugars, furans, and nitrogen compounds. The phenolic compounds (phenol, guaiacol and other substituted phenol compounds)are formed by decomposition of lignin. Phenols have received considerable attention because of their low reactivity in HDO process. (Bu et al. 2012)

The hydrogenation of phenol has been reported to take place over palladium (Echeandiaet al. (2014), de Souza et al. (2015), Talukdaret al. (1993), Zhao et al. (2011)), nickel (Echeandia et al. (2010), Gandarias et al. (2008), Kallury et al. (1984), Platanitis. et al. (2014), Ryymin et al. (2010), Senol et al. (2007), Shinand Keane (2000), Yoosuk et al. (2012), Zhang et al. (2013)) and cobalt (Badawi et al. (2013), Platanitis et al. (2014), Senol et al. (2007)) based catalysts. It is reported that phenol hydrodeoxygenation reaction occurs via two pathways: The one pathway comprises the hydrogenation (HYD) of phenolic aromatic ring leading to formation of cyclohexanol, cyclohexanone, cyclohexene and cyclohexane while the second pathway follows the direct deoxygenation (DDO) including the direct cleavage of the C-O bond and leading to benzene, cyclohexene and cyclohexane formation. Methyl-cyclopentane (Echeandia et al.,

2010), and compounds formed from the coupling of two phenol-derived units leading to C12 oxygenated compounds (Kallury et al. (1984), de Souza et al. (2015)) have been also reported as products.

The main objective of this work is the kinetic study of the liquid-phase catalytic hydrodeoxygenation of phenol which is a representative model compound of bio-oil. The experiments were conducted over a commercial NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst that is mainly used for hydrotreatment of petroleum fractions.

### Experimental

The experiments were carried out in a mini scale unit. A spiral string bed reactor with 2.1 mm internal diameter was used. The reactor was loaded with 0.25 gr of the crushed commercial NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with dimensions in the range 0.160-0.315 mm. The liquid feed consisted of 1% wt phenol diluted in ndodecane. The solvent was selected to ensure low volatility and enables the study of phenol hydrogenation in liquid phase within the range of the conditions tested. Three liquid feed rates were tested corresponding to WHSVs from 11 up to 32 h<sup>-1</sup>. The experiments were performed at three pressures 20, 30 and 40 bar, and four temperatures within the range 130-170°C. The H<sub>2</sub> feed rateswere high enough to ensure absence of restrictionof external mass transfereffects.

Benzene and cyclohexanol hydrotreatment experiments were also performed at the same conditions in order to clarify the reaction scheme for the phenol hydrodeoxygenation over the NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. All chemicals were of hight purity >99% obtained from commercial suppliers.

Standard experiments were repeated at regular time intervals for the determination of the catalyst

<sup>•</sup> To whom all correspondence should be addressed have also been reported as products.

activity level. The analysis of the samples was conducted by gas chromatography, using n-heptane as internal standard. The catalyst was reduced inhydrogen atmosphere and the thermo-program reached a maximum temperature of 350 °C.

#### **Experimental Results**

Thermodynamic calculations indicated negligible evaporation of the components in the separator, and thus the measured concentrations at the separator outlet correspond to the liquid phase components concentration at the reactor outlet. The cyclohexene yield in the range of the conditions tested was lower than 2% and two main products were detected: cyclohexanol and cyclohexane. In Figure 1, the yield of the two main products is presented, for the liquid flow rates and temperatures tested at pressure 30 bar.

The yieldis defined with the following equation Eq. (1):



Figure 1. Yield of A) cyclohexanol and B) cyclohexane. Pressure :30 bar.

At high feed flow rates and low temperatures cyclohexanol is the main product. The cyclohexane yield increases with temperature and decreases with WHSV increase.

In Figure 2, the yield of cyclohexane and cyclohexanol is presented, for the liquid flow rates and

pressures tested at temperature145 °C. From the data presented in this Figure it is clear that the yield is not strongly affected by the pressure, and small changes with pressure are observed.



Figure 2.Yield of A) cyclohexanol and B) cyclohexane. Temperature :145 °C.

# **Kinetic Model**

The overall reactions indicated by our results for phenol hydrodeoxygenation over the NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst can be represented by a two pathways scheme: (I) the direct deoxygenation of phenol to benzene which consequently is fully hydrogenated to cyclohexane, and (II) the hydrogenation (HYD) of phenol's aromatics to cyclohexanol and the gradual formation of cyclohexene and cyclohexane, according to the following scheme 1.



Scheme 1. Reaction scheme for phenol hydrogenation over  $NiMo/\gamma$ -Al<sub>2</sub>O<sub>3</sub>catalyst, for the conditions tersted.

The rate equations for each reaction path considered are presented in the following equations Eq. (2) - Eq. (4).

$$R1 = k1 \exp(\frac{-Ea1}{RT}) C_{ph}^{n1} P^{m1}$$
(2)

$$R2 = k2\exp(\frac{-Ea2}{RT})C_{ph}^{n2}P^{m2}$$
(3)

$$R3 = k3 \exp(\frac{-Ea3}{RT}) C_{c-ol}^{n3} P^{m3}$$
(4)

where C stands for concentration, P for hydrogen pressure while the indicator ph represents phenol and c-ol cyclohexanol.

A plug flow model was considered for the catalyst bed. A homemade code, which incorporates the Runge-Kutta 4th order method for the solution of the differential mass balances along the bed and the Nelder-Mead Simplex optimization method was used for the kinetic parameters estimation. In Table 1, the estimated kinetic parameters are presented.

Table1. Estimated kinetic parameters. The preexponential factors ki are expressed in units  $(gr_{feed})^{ni}mol^{(1-ni)}bar^{-mi}gr_{cat}^{-1}h^{-1}$  and the activation energies Eai in kJmol<sup>-1</sup>.

k1	5.14x10 <sup>11</sup>	Ea1	123	n1	0	m1	0.06
k2	5.82x10 <sup>5</sup>	Ea2	59	n2	0.46	m2	0.67
k3	2.25x10 <sup>15</sup>	Ea3	134	n3	0.56	m3	0.092

The parity plot of the calculated and experimental phenol conversion and product yields using the estimated kinetic parameters in Table 1 are presented in Figure 3. In this Figure the yield is based on the inlet phenol concentration. It is observed that the model fits satisfactorily to the experimental data.



Figure 3. Parity plot of experimental and calculated phenol conversion and products yield. Kinetic parameters of Table 1.

The kinetic model for cyclohexanol hydodeoxygenation was verified by conducting experiments at the same conditions that the phenol experiments were conducted, using as feed a mixture of 1.06% w/w cyclohexanol in n-dodecane. Running the simulation codes only for cyclohexanol HDO and using the kinetic parameters for cyclohexanol presented in Table 1, the kinetic model fits satisfactorily to the experimental results, as presented in Figure 4.



Figure 4. Parity plot of experimental and calculated cyclohexanol conversion. Cyclohexanol hydrodeoxygenation experiments. Kinetic parameters for cyclohexanol in Table 1.

# Conclusions

The main products of the phenol hydrotreatment over a commercial NiMo/y-Al2O3 catalyst in the range of the conditions tested, are cyclohexanol, cyclohexane, cyclohexene and traces of benzene. The cyclohexene yield in the range of the conditions tested was lower than 2%. At high feed flow rates and low temperatures cyclohexanol is the main product. The cyclohexane yields increases with temperature and decreases with pressure and WHSV increase. The study of products hydrotreatment at the same experimental conditions indicate that phenol hydrodeoxygenation reaction over the NiMo/y-Al<sub>2</sub>O<sub>3</sub> catalyst occurs via a two parallel pathways, as already mentioned in literature: (I) the direct deoxygenation of phenol (DDO) to benzene which consequently is hydrogenated to cyclohexane, and (II) the hydrogenation (HYD) of phenol's ring to cyclohexanol followed by deoxygenation forming gradually cyclohexene and cyclohexane. The rate of the direct deoxygeanation path (I) is low while the benzene hydrogenation to cyclohexane reaction is very fast. Phenol conversion proceeds mainly by the pathway II (HYD). The developed kinetic model for the phenol conversion to the products fits satisfactorily to the experimental data.

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# EXPERIMENTAL STUDY OF CATALYTIC COATING FOR REDUCED COKE FORMATION

Stamatis A. Sarris<sup>a</sup>, Carl M. Schietekat<sup>a</sup>, Lawrence B. Kool<sup>b</sup>, Wenqing Peng<sup>b</sup>, Patrick Lucas<sup>b</sup>, Kevin M. Van Geem<sup>a</sup>, Guy B. Marin<sup>a</sup>

<sup>a</sup> Ghent University, Laboratory for Chemical Technology, Technologiepark 914, 9052 Gent, Belgium.

<sup>b</sup>GE Global Research, Niskayuna, New York and Shanghai, China.

### Abstract

A novel catalytic coating, called "YieldUp", that gasifies coke to carbon oxides by reaction with steam, was developed for application on the inner wall of steam cracking reactors. Experimental evaluation of three different coating formulations was conducted in a jet stirred reactor setup during steam cracking of ethane. The results showed drastic decrease of the coking rates compared to a reference alloy, combined with increased CO and  $H_2$  yields, due to gasification of coke. Scanning electron microscope (SEM) and energy diffractive X-ray (EDX)surface and cross-section analyses were conducted to evaluate further the formulations. The results showed good adhesion of the coating to the base alloy even after several coking/decoking cycles and that the stable anti-coking behavior is strongly dependent on the oxide layer and catalytic coating thickness distribution.

### Keywords

Steam cracking, thermal cracking, ethane, coke formation, catalytic coating, jet stirred reactor

### Introduction

Steam cracking of hydrocarbons is the dominant process to manufacture light olefins. Coke deposition on the inner wall of the tubular reactors of steam cracking units affects negatively the economics of the steam cracking process. As coke is formed, the crosssectional area of the reactor decreases, leading to an elevated pressure drop over the reactor. Higher pressures favor bimolecular reactions - responsible for a.o. formation of aromatics -over monomolecular reactions, leading to shifts in product selectivities. In addition, the thick coke layer hinders the heat transfer from the furnace to the reactors. To compensate for this extra conductive heat transfer resistance and to keep a constant severity over operation, the fuel flow rate to the furnace burners is increased resulting in a reactor tube metal temperature rise. At the point that the maximum allowed metallurgical temperature for the tube is reached, around 1400 K or when the reactor pressure drop surpass a predefined operational maximum value, the reactors are decoked online by feeding steam or - more commonly - a steam/air mixture. The decoking procedure typically runs for at least 48h reducing the yearly production capacity and having a negative impact on operating costs. Many anti-coking technologies have been developed and applied commercially over the last years. Spontaneously, these technologies can bedivided into three classes: three-dimensional (3D) reactor technologies, feed additives and surface technologies.

• To whom all correspondence should be addressed: Prof. dr. ir. Kevin M. Van Geem, Kevin.VanGeem@UGent.be

In 3D reactor technologies, the reactor tube geometry is altered from the conventional bare, straight tube to a more complex geometry to enhance convective heat transfer and/or increase heat transfer area. For example finned tubes <sup>8, 10, 26</sup>, ribbed <sup>29</sup> or

partially ribbed <sup>15</sup> tubes and swirl flow tubes <sup>26</sup> have been investigated. All these technologies lead to an increased pressure drop compared to conventional bare tubes and hence affect the ethene selectivity <sup>27</sup>. The second category is the most widely applied techniques . For some additives a combination of pretreatment and continuous addition is applied, while for others only continuous addition is beneficial. Sulfur-containing compounds are the most commonly applied group of additives <sup>1-4, 9, 11, 25, 32, 33</sup>. The role of sulfur additives on diminishing carbon monoxide formation is well established, but their effect on coke formation is debated <sup>31</sup>. Besides sulfur-containing additives, components with phosphorus <sup>13, 30, 31</sup> and silicon <sup>7, 33</sup> have also been investigated. The surface technologies category includes high performance alloys, application of coatings and pretreatments. Steam cracking reactors are typically made out of heat-resistant Fe-Ni-Cr alloys which resist coke formation by an oxide layer of chromia 16, 17. Often aluminum and manganese are added to enhance the coking resistance of the alloys by forming a protective alumina or a manganese chromite (MnCr<sub>2</sub>O<sub>4</sub>) spinel layer respectively<sup>16, 17</sup>. Alternatively, a thin layer of a coating is deposited on the reactor base alloy surface. Distinction can be made between barrier coatings that passivate the inner wall and catalytic coatings <sup>22</sup> that convert coke to carbon oxides. A barrier coating pacifies the base alloy by covering the catalytically active sites, eliminating catalytic coke formation. However, the non-catalytic coke formation through a free-radical mechanism - often termed pyrolytic coke- is not reduced. In contrast, catalytic coatings eliminate the base alloy catalytic coke formation by covering the base metal active sites and provide catalytic sites for converting radically formed coke to carbon oxides and hydrogen by reaction with steam via gasification reactions.

Several authors have investigated the application of barrier coatings in steam cracking reactors. Zychlinski et al. <sup>34</sup> tested the performance of the AlcroPlex<sup>®</sup>

coating (Al/Si barrier coating) in an electrobalance setup. This coating decreases the total coke deposition up to 90 % when cracking ethane and up to 80 % when cracking naphtha compared to a reference HP 40 material. Ganser et al. <sup>12</sup> described the application of AlcroPlex<sup>®</sup> in an industrial ethane cracker. The run length of the furnace was increased from 30 days to more than 60 days after installation of coated tubes. Additionally, lower CO yields were measured and decoking operation was accomplished in less than half the normal time. No carburization of the tubes was seen and the coating seemed essentially unchanged after one year.

NOVA Chemicals and Kubota have developed a technology - commercialized as ANK 400 - to reduce both catalytic and pyrolytic coke <sup>5, 14</sup>. The heat resistant base alloy is separated from the process gas with a micron-sized inert manganese chromium oxide ANK 400 spinel. Application of fresh ANK400 tubes in two ethane-cracking furnaces resulted in an increase of the run length from 33 to more than 400 days. Subsequent runs had a duration of around 175 days. Westaim Surface Engineered Products developed another barrier coating, called CoatAlloy 6, 21, 24. CoatAlloy consists of an engineered surface, an enrichment pool and diffusion barriers coated on the bulk alloy. In the original patent <sup>18</sup>, the intermediary diffusion barrier is an aluminum-containing coating deposited directly onto the bulk alloy substrate prior to deposition of the enrichment pool. The enrichment pool is a MCrAlX material in which M is nickel, cobalt, iron or a mixture thereof and X is yttrium, hafnium, zirconium, lanthanum or a combination thereof. This enrichment pool heat-treated to bond the coating to bulk alloy and to form a multiphasic microstructure. The overlay coating is then aluminized by depositing a layer of aluminum and oxidizing the resulting coating to form an alumina surface layer. Between 1995 and 2001 several improvements have been made to the technology resulting in an increased operating limit from 1293 K (Original CoatAlloy<sup>TM</sup>) to 1333 K (CoatAlloy<sup>TM</sup> - 1060) and 1373 K (CoatAlloy<sup>TM</sup> -1100)<sup>24</sup>. By 2001, CoatAlloy coatings were installed in 25 furnaces globally and typically resulted in a decrease in coking rate by about 90 % <sup>24</sup>.

Besides the inert barrier coatings, several catalytic coatings have also been developed. The so-called Catalyzed-Assisted Manufactrure of Olefins (CAMOL) coating was developed by Quantiam Technologies and Nova Chemicals from 2001 to 2008 and is since 2011 commercialized by BASF Qtech <sup>19, 22</sup>. Two families of coatings have been developed; one manganese and one tungsten based <sup>20</sup>. As such two products are commercially available: the Low-Catalytic Gasifier (LCG) and the High-Catalytic Gasifier (HCG) <sup>23</sup>. The LCG can be used for ethane-propane cracking, while the HCG coating targets at heavier feedstocks cracking such as naphthas. The coatings have been installed in an industrial naphtha-cracking furnace. After three years in operation, it was found that modified start up

procedures are required in order to reactivate the catalytic sites <sup>23</sup>. A small amount of HCG was coated on the reactors' outlet tubes. Before application of the coating, the furnace was typically limited by high outlet TMT's. However, with the help of this small amount of HCG, the furnace became pressure drop limited instead <sup>23</sup>. This shows that only a small amount of HCG can gasify a significant amount of coke. A sample taken from a reactor after 14 months of service showed minor damage to the coating which could be repaired after an oxidation procedure <sup>23</sup>.

SK-corporation developed a method of on-line coating the reactor inner walls with a catalytic film, called PY-COAT <sup>28</sup>. The method comprises three steps of vapor depositing: a solution of a metal alkoxide and a chromic compound to form a buffer layer on the inner walls; a metal alkoxide as a barrier on the buffer layer and finally an alkali metal/alkaline earth metal compound alone or mixed with metal alkoxides as a decoking layer on the barrier. Application in a Millisecond naphtha-cracking furnace more than doubled the run length.

In the following, a new catalytic coating, called YieldUp, is presented. The coating is based upon a family of ceramic catalysts having doped perovskite structures that are capable of converting coke to carbon oxides and hydrogen. The performance of different formulations of this coating was probed in a jet stirred reactor (JSR) setup. Finally, the studied formulations were evaluated and studied by means of SEM and EDX.

# **Experimental results**

The application of the YieldUp catalytic coating on product yields and coke formation was assessed in the JSR setup. Three different YieldUp formulations were tested and compared to the reference Incoloy 800HT alloy. The conversion of ethane amounted to about 70 wt% and the yields of ethene and propene were about 50.5 wt% and 0.78 wt% respectively. The yields of hydrogen and carbon oxides were significantly increased by application of the YieldUp1 formulation. The yields of other components are not influenced by the coating or differences are within the experimental error. The amount of coke deposited on the coupon was significantly decreased in all cycles by application of all coating formulations compared to the reference Incoloy 800HT alloy. The lower amount of deposited coke results in higher carbon oxides and hydrogen yields in the YieldUp1 experiment as part of the coke formed on the coating is gasified. This holds to a lesser extent for YieldUp2 and YieldUp3 as for these coating formulations less coke is gasified. The coking data together with the process conditions obtained in the JSR set-up are summarized in Table 1.

 Table 1. Process conditions and coking results of ethane

 cracking in the JSR

Coupons	Incoloy	YieldUp	YieldU	YieldU
	800HT	1	p2	p3

Temperature	1159	1159	1159	1159	
[ <b>N</b> ] Fthane flow					
rate $[10^{-6} \text{ kg/s}]$	33.3	33.3	33.3	33.3	
Steam flow					
rate $[10^{-6} \text{ kg/s}]$	11.1	11.1	11.1	11.1	
Dilution	0.33				
[Kg/Kg]	60.34	70.33	60 11	60 47	
[wt%]	09.34	70.55	09.44	09.47	
Mass of coke					
[10 <sup>-6</sup> kg / 6h]					
1 <sup>st</sup> cycle	39.0	5.0	10.0	10.2	
2 <sup>nd</sup> cycle	42.5	6.5	12.0	11.3	
3 <sup>rd</sup> cycle	45.0	9.0	17.2	12.6	
$\begin{array}{c} R_{c,init.}  [10^{-6}] \\ kg/s/m^2] \end{array}$					
R <sub>c,init.</sub> [10 <sup>-6</sup> kg /s/m <sup>2</sup> ]					
$\frac{R_{c,init.}}{kg / s/m^2]} \begin{bmatrix} 10^{-6} \\ \end{bmatrix}$	22.4	2	5.3	5.8	
R <sub>c,init.</sub> [10 <sup>-6</sup> kg /s/m <sup>2</sup> ] 1 <sup>st</sup> cycle 2 <sup>nd</sup> cycle	22.4 19.2	2 2.3	5.3 7.2	5.8 5.80	
Rc,init.         [10 <sup>-6</sup> kg /s/m²]         1 <sup>st</sup> cycle           2 <sup>nd</sup> cycle         3 <sup>rd</sup> cycle	22.4 19.2 19.1	2 2.3 2.4	5.3 7.2 10.2	5.8 5.80 7.70	
$\begin{array}{c c} \mathbf{R}_{c,init.} & [10^{-6}\\ \mathbf{kg} / \mathbf{s} / \mathbf{m}^2] \end{array}$ $1^{st} cycle$ $2^{nd} cycle$ $3^{rd} cycle$ $4^{th} cycle$	22.4 19.2 19.1 19.10	2 2.3 2.4 4.1	5.3 7.2 10.2 5.3	5.8 5.80 7.70 5.20	
Rc,init.         [10 <sup>-6</sup> kg /s/m²]         1 <sup>st</sup> cycle           2 <sup>nd</sup> cycle         3 <sup>rd</sup> cycle           4 <sup>th</sup> cycle         4 <sup>th</sup> cycle           Rc,asym.         [10 <sup>-6</sup> kg/s/m²]         [10 <sup>-6</sup>	22.4 19.2 19.1 19.10	2 2.3 2.4 4.1	5.3 7.2 10.2 5.3	5.8 5.80 7.70 5.20	
Rc,init.         [10 <sup>-6</sup> kg /s/m²]         1 <sup>st</sup> cycle           1 <sup>st</sup> cycle         3 <sup>rd</sup> cycle           3 <sup>rd</sup> cycle         4 <sup>th</sup> cycle           Rc,asym.         [10 <sup>-6</sup> kg/s/m²]         1 <sup>st</sup> cycle	22.4 19.2 19.1 19.10 4.0	2 2.3 2.4 4.1	5.3 7.2 10.2 5.3	5.8 5.80 7.70 5.20	
Rc,init.         [10 <sup>-6</sup> kg /s/m²]         1 <sup>st</sup> cycle           2 <sup>nd</sup> cycle         3 <sup>rd</sup> cycle           4 <sup>th</sup> cycle         Rc,asym.           Rc/s/m²]         1 <sup>st</sup> cycle           1 <sup>st</sup> cycle         Rc,asym.	22.4 19.2 19.1 19.10 4.0 6.1	2 2.3 2.4 4.1 0.9 1.2	5.3 7.2 10.2 5.3 1.0 1.9	5.8 5.80 7.70 5.20 1.1 1.5	

The surface and cross-section coating morphology and composition are evaluated for the different formulations by means of SEM and EDX analysis. The results revealed that the catalytic layers consisted mainly of barium, cerium, zirconium and oxygen. The thickness of the layers varied between 15 µm and 30 um, adhered to the base via an oxide layer, which contained both elements from the alloy and the coating. "YieldUp1" proved to have a very porous layer, while the other two formulations were denser. In Figure 1, elemental mapping of cross-section analyses of the coke coupons of the three formulation are illustrated. Based on that, the thickness distribution of the oxide layer and the coating formulation seems to be a substantial parameter affecting the anti-coking technology.



Figure 1. Elemental mappings of cross sections of coked coupons of YieldUp1 (top), YieldUp2 (middle) and YieldUp3 (bottom).

# Conclusions

Three different formulations of a novel catalytic coating, called YieldUp, were evaluated in a Jet Stirred Reactor. To fundamentally understand their coking performance difference, the coked coupons were further evaluated with SEM and EDX analysis. Overall, the results indicated that:

- coking rates decreased by a factor of at least 3 in comparison with the reference material
- the yields of CO and CO<sub>2</sub> were significantly increased indicating that the coating is probably too active under the studied conditions
- the best anti-coking behavior was observed in the formulation that had the highest porosity, since more carbon could interact with the catalytic coating, driven to gasification
- more equally distributed oxide layers and catalytic coating thickness's lead to lower coking rates and reduced aging
- more research is needed towards the gasification reactions occurring on the coating to further tune the coating's activity

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# Application of montmorillonite-Cu(II)ethylenediamine catalyst for the decolorization of Chromotrope 2R with H<sub>2</sub>O<sub>2</sub> in aqueous solution

Ibrahim A. Salem\*, Hoda A. El-Ghamry, Marwa A. El- Ghobashy

Chemistry Department, Faculty of science, Tanta University, Tanta 31527, Egypt

# Abstract

The kinetics of decolorization of Chromotrope 2R (C2R) was studied spectrophotmetrically using the montmorilloniteK10-Cu(II)ethylenediamine composite (MMTK10-Cu(en)<sub>2</sub>) as catalyst and H<sub>2</sub>O<sub>2</sub> as oxidant in aqueous solution. The catalyst was prepared and characterized by SEM, FTIR, XRD and TGA techniques. The dependence of reaction rate on H<sub>2</sub>O<sub>2</sub> concentration was examined under UV irradiation in the presence and absence of the catalyst, and in the presence of the catalyst without the UV irradiation. In all these reaction systems, the rate increased up to a maximum value and then decreased. The rate increased with the increase in the concentration of the dye reaching a maximum. The amount of the catalyst and the effect of the temperature showed significant increase in the decolorization rate. The addition of NaCl to the reaction medium has accelerated the rate effectively. A similar catalyst, MMTKSF-Cu(en)<sub>2</sub>, has also been employed and was found to be less efficient compared with MMTK10-Cu(en)<sub>2</sub>.

*Keywords:* Montmorillonite, Copper(II)-ethylenediamine complex, Chromotrope 2R, H<sub>2</sub>O<sub>2</sub>, Textile dyes, Decolorization.

<sup>\*</sup> Corresponding author Tel: 0020403305978

Email address: dr.ibrahimsalem@science.tanta.edu.eg

# STATIC AND DYNAMIC STUDY OF ALKENE CRACKING INTERMEDIATES IN H-ZSM-5

Pieter Cnudde, Jeroen Van der Mynsbrugge, Kristof De Wispelaere, Karen Hemelsoet, Michel Waroquier, Veronique Van Speybroeck Center for Molecular Modeling, Ghent University, Technologiepark 903, Zwijnaarde, Belgium

# Abstract

To meet the annually increasing propylene demand, on-purpose technologies such as olefin cracking processes are expected to become economically interesting. In this contribution, monomolecular cracking on H-ZSM-5 of butene as a model component is studied using static and dynamic computational modeling techniques. A thorough understanding of the reactive intermediates is required to calculate the kinetics of this process. Although a carbenium ion-based mechanism is generally accepted, the discussion about the precise nature and stability of the reaction intermediates is ongoing. A key question is whether carbenium ions are long-lived species in the zeolite pores or will quickly rearrange to a more stable state such as a framework-bound alkoxide or a physisorbed  $\pi$ -complex. Static calculations predict the 2-butoxide to be more stable than the 1-butene  $\pi$ -complex, which is in turn more stable than the 2-butyl carbenium ion. However, a complete characterization of the intermediates in a high-temperature process cannot be made by static modeling alone. Molecular dynamics simulations, which fully account for conformational entropy and temperature effects, show that 2-butoxide is less stable than expected by static calculations and that it is prone to rearrangements. The t-butyl cation is found to be more stable compared to t-butoxide, which is not inconsistent with static predictions.

#### Keywords

Alkene cracking, molecular modeling, carbenium ions, alkoxides, zeolites

### Introduction

Light olefins such as propylene and ethylene remain to date the most important base chemicals. Because of the rapidly increasing propylene demand, so-called on-purpose producing technologies such as methanol-to-olefins (MTO) and olefin cracking are receiving considerable attention and are expected to become economically viable in the near future. (Chen et al. 2005) Conversion of excess  $C_4 - C_8$  alkenes on acidic zeolite catalysts plays a crucial role in these processes.

It is generally accepted that cracking reactions occur through a carbenium ion mechanism. (Buchanan et al. 1996, Kissin 2001) A profound insight in the nature and stability of the reactive intermediates is required to determine accurate kinetics for these reactions. However, the question remains whether carbenium ions remain long-lived inside the zeolite pores or rapidly evolve either by deprotonating to a  $\pi$ complex or by forming a stable framework-bound alkoxide (see Figure 1). Due to the short lifetime of simple alkyl carbenium ions, experimental observation is difficult. (Haw et al. 1996) Previous theoretical studies indicated the high stability of primary and secondary alkoxides. (Rigby et al. 1997, Mazar et al. 2013)

Several theoretical studies have focused on the protonation of isobutene and the formation of a tertiary butoxide or a tertiary butyl carbenium ion. (Nguyen et al. 2012, Tuma and Sauer 2005) Carbenium ion stability was found to depend mainly on the interplay between stabilizing electronic effects and destabilizing steric constraints introduced by the zeolite pore dimensions. For H-ZSM-5, it was suggested that due to the large entropy loss upon alkoxide formation, the tbutyl cation becomes the most stable species at temperatures of 500K or higher. (Nguyen et al. 2012)



Figure 1. Three possible adsorption states for a linear butyl chain: a butyl carbenium ion (above), a physisorbed π-complex (left) and a 2-butoxide (right)

A butene molecule can undergo either immediate  $\beta$ -scission into two ethylene species, which is called monomolecular cracking, or dimerizationcracking. (Abbot et al. 1985) In this contribution, monomolecular cracking of 1-butene on the industrially important H-ZSM-5 catalyst is considered. First, the free energy profile for 1-butene cracking is constructed based on static calculations Secondly, molecular dynamics simulations are performed to observe the behavior of several linear and branched C<sub>4</sub> intermediates at actual cracking temperatures and attain a more detailed understanding of their relative stability.

### Methodology

To evaluate the butene  $\beta$ -scission free energy profile, static calculations on a 46T-cluster model of H-ZSM-5 are performed. For computational efficiency, all geometries are optimized with the 8T:46T ONIOM(B3LYP/6-31+g(d,p):pm3) scheme. The IRC method is applied to locate the reactant and product minima adjacent to the transition state. Single point energy calculations at the  $\omega$ B97X-D level of theory are performed on the optimized structures. Geometry optimizations, frequency calculations and single-point energy refinements are performed with the Gaussian09 software. (Frisch et al. 2009) Free energies corrections based on harmonic oscillator approximation are obtained with the TAMkin package. (Ghysels et al. 2010)

To study the dynamic behavior of the intermediate species in the zeolite channels, ab initio molecular dynamics (MD) simulations are carried out on a periodically extended H-ZSM-5 unit cell. The Brønsted acid site is situated at the intersection of the straight and sinusoidal channel. Electronic energies are evaluated at the revPBE level of theory with additional Grimme D3 dispersion corrections in the DZVP-GTH basis set. Statistical sampling with a timestep of 0.5 fs is performed in the NVT ensemble at a temperature of 500°C, controlled by a chain of five Nosé-Hoover thermostats. To eliminate effects of the initial geometry, an equilibration run of 5 ps is performed, followed by a 40 ps production run. The CP2K software package (Van de Vondele et al. 2005) is used for molecular dynamics simulations.

#### **Results and Discussion**

#### Static Calculations

Based on the successful application of the 46T-cluster model for the description of methylation reactions in previous work by Van Speybroeck et al. (2011), the same zeolite model is used to study the monomolecular cracking of 1-butene.

The only monomolecular cracking pathway towards lighter olefins is  $\beta$ -scission through a primary 1-butyl cation. The free energy profile for this scission, obtained from static cluster calculations is shown in Figure 2. The optimized transition state geometry is displayed in Figure 3. The transition state of this reaction resembles the product state: a formal primary ethyl cation is being formed, while C1 and C2 transform into  $sp^2$  hybridization. The cracked products of this  $\beta$ scission are ethylene and an ethyl carbenium ion. The latter is a very unstable species and immediately stabilizes by covalently bonding to the framework, forming an ethoxide. The small ethylene fragment shows little interaction with the zeolite wall and tends to diffuse away from the active site during product optimization. Although, a primary 1-butyl cation could be expected as a pre-reactive complex for this  $\beta$ scission, this species is not retrieved as a minimum on

the potential energy surface (PES). A spontaneous isomerization of the 1-butyl carbocation to the more stable linear 2-butyl carbocation takes place during the geometry optimization through a seemingly barrierless hydride shift over a protonated cyclopropyl state.



Figure 2. Free energy diagram for 1-butene cracking with indication of the three possible adsorption states and 1-butene in gas phase as reference level

Prior to cracking, 1-butene adsorbs at a Brønsted acid site, forming either a physisorbed  $\pi$ -complex, a carbenium ion or a framework-bound butoxide. The free energies of these species are also given in Figure 2. Although the 2-butyl cation appears to be a local minimum on the PES, this species has a considerably higher free energy (+75 kJ/mol) than the physisorbed  $\pi$ -complex (+23 kJ/mol) and the 2-butoxide (-36 kJ/mol). Based on these calculations, it can be expected that a 2-butyl carbenium ion will bind to the framework to form a more stable 2-butoxide and that the latter will be the most prevalent species. (Boronat and Corma 2008, Nguyen et al. 2012)



Figure 3. Optimized geometry of the 1-butene cracking transition state

An important concern is how to connect the computed free energy profile to experimentally observed activation energies. In Figure 2, the three activation barriers are indicated with different indices. Depending on the level selected as the reactant state, very different estimates for the activation energy are obtained. The intrinsic activation barrier from the butyl cation ( $\Delta G^{\dagger}_{int}$ ) amounts to 81 kJ/mol, while the barrier with respect to the physisorbed  $\pi$ -complex ( $\Delta G^{\dagger}_{phys}$ ) has a value of 133 kJ/mol and the barrier with respect to the chemisorbed butoxide ( $\Delta G^{\dagger}_{chem}$ ) equals 192

kJ/mol. This result is in agreement with the prediction by Sun et al. (2010). Given that 2-butoxide is the most stable state, a high activation barrier for cracking is expected. Therefore, a correct assessment of the relative stability of the various intermediates is of paramount importance. To investigate whether the stability and free energies of these intermediate states are correctly estimated from our static calculations, molecular dynamics simulations are performed, which allow characterizing the dynamic behavior of these species.

#### MD simulations

In static calculations, free energy barriers are computed by subtracting the free energies of a local minimum and a local saddle point. A general limitation of this approach is that only a single point on the free energy surface is considered, which corresponds to a single geometry and configuration. Depending on the selection of those local minima, different activation barriers could be obtained. (Bucko et al. 2011) At high temperature, the species usually possesses sufficient thermal energy to allow quick rearrangements to other configurations. For evaluating thermodynamic and kinetic properties, the entire distribution of different conformers with slightly different energies should be taken into account. Furthermore, static geometries are optimized on the potential energy surface at 0 K, while at finite temperature entropy effects may have a significant influence on the resulting geometries and energies. By performing MD simulations, the free energy surface is sampled, taking finite temperature effects and conformational flexibility of the adsorbed species inherently into account.

The dynamic behavior of several C<sub>4</sub> species at 500°C is investigated. First, the 2-butyl carbenium ion is simulated. The simulations reveal a rapid transition from the secondary carbenium ion to a physisorbed butene  $\pi$ -complex. Deprotonation to the active site of the framework occurs within the equilibration run. Once a deprotonation (shown in Figure 4) has occurred, the butene molecule is not protonated again in the course of the production run.



Figure 4. Snapshot of a deprotonation transition of 2butyl carbenium ion into 2-butene

Three independent simulations with different starting geometries yield the same result, indicating that this observation is not merely coincidental. A 2-butyl carbenium ion species is thus expected to be a shortlived intermediate with a low probability to occur in the zeolite environment. Interestingly, the formation of a 2-butoxide was not observed.

Subsequently, the 2-butoxide species is simulated. In contrast to what might be expected from the static calculations, the covalent bond with the framework is already broken within the equilibration run. To enforce equilibration of the 2-butoxide, a parabolic constraint, centered at an average C-O distance of 1.6 Å (see Figure 5) has to be imposed. Upon removal of the constraint after 20 ps simulation time, the 2-butoxide again forms a 2-butyl cation, which deprotonates within 5 ps. These observations indicate that the covalent bond with the framework introduces an entropic penalty that destabilizes the 2butoxide. The 2-butoxide state will thus only rarely exist, in contrast to the conclusion of the static results.



Figure 5. Distribution of the distance of the adsorbate to the acid site in Ångström: C<sub>1</sub>-O distance in 1-butene (red), C<sub>2</sub>-O distance in 2-butoxide (blue) and C<sup>+</sup>-O distance in t-butyl cation (green)

Thirdly, the 1-butene  $\pi$ -complex is investigated. At 500°C, this intermediate is a quite stable state, which is sampled during a large part of the production run. Regular transitions between the  $\pi$ complex and a more freely adsorbed 1-butene state are observed, which is likely due to a small disfavorable entropic effect associated with the interaction of the double bond with the acid site. This is illustrated by the quite broad distribution of the C-O distance in Figure 5. After ca. 25 ps simulation time, the butene fragment even tends to diffuse away from the active site.

To assess the effect of branching, the t-butyl cation has also been simulated. The stability order appears to be different for the branched adsorbate. The tertiary t-butyl carbenium ion was found to be stable during the entire production run, remaining in the neighborhood of the acid site at an average distance of 4.25Å. (Figure 5)

Next, the isobutene  $\pi$ -complex was studied. At the end of the equilibration run, isobutene rearranged to

a t-butyl carbenium ion, confirming the higher stability of a tertiary over a secondary carbenium ion. During the production run, a rare deprotonation into isobutene occurred. Isobutene was sampled for a few picoseconds before getting reprotonated into the t-butyl cation.

Finally, a t-butoxide was simulated. The tertiary butoxide is less stable than the secondary butoxide since desorption from the framework into the t-butyl cation takes place instantaneously at the start of the simulation. Again, equilibration was enforced by imposing a parabolic constraint on the C-O distance. Upon withdrawal of the constraint, immediate formation of the t-butyl carbenium was again observed. These results are in good agreement with the predictions of Nguyen et al. (2011) and Nieminen et al. (2005).



Figure 6. Distribution of the  $C_1C_2C_3C_4$  dihedral angle for 1-butene (red), 2-butoxide (blue) and t-butyl cation (green)

Finally, note that several configurations of the simulated species are effectively sampled as shown by the dihedral angle distributions in Figure 6. The 2-butoxide species has the least configurational freedom, followed by the t-butyl carbenium ion, while the 1-butene species shows the broadest distribution of conformers. The distributions of the butene and t-butyl species are quite flat, indicating that all different conformers contribute to the adsorbent properties and that it is indeed necessary to take all configurations into account instead of singling out one geometry.

# Conclusion

To accurately determine the kinetics for butene cracking, a thorough understanding of the nature and stability of the reaction intermediates is required. Static modeling predicts the frameworkbound 2-butoxide to be the most stable state and therefore the most prominent reaction intermediate of the three possible linear C<sub>4</sub> species, followed by the 1butene  $\pi$ -complex and the 2-butyl carbenium ion. Molecular dynamics simulations at 500°C confirm that physisorbed 1-butene is a stable state, while the 2-butyl cation is prone to rearrangements. However, 2butoxide appears to be less stable than was found statically. The 2-butyl cation stabilizes into a physisorbed  $\pi$ -complex instead of forming a butoxide. In MD simulations, conformational freedom and finite temperature effects are inherently included, while static calculations consider only a single minimum on the potential energy surface, without taking entropy into account. Clearly, the free energies of the intermediates are not calculated correctly using the static approach at these reaction conditions. Regarding isobutene intermediates, MD simulations confirm the long-lived character for the t-butyl cation, which is energetically favored over a framework-bound t-butoxide, a result that is in good agreement with previous predictions using static modeling.

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# THE DECOMPOSITION OF HYDROXYAMYL AND PENTYLOXY RADICALS OF 2-METHYL-1-BUTANOL: A THEORETICAL STUDY

Xueyao Zhou, Xiaoyuan Zhang and Lidong Zhang\*

National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, P.

R. China

### Abstract

2-Methyl-1-butanol is one of the good substitute fuels with high energy density, low water solubility and well miscibility with practical fuels. In the present works, main radicals isomerization and unimolecular decomposition reactions pathways were investigated by CBS-QB3 method. For the main pathways were also calculated at QCISD(T)/CBS//M062x/cc-pvtz level. Major isomerization and decomposition reactions channels were discussed based on the potential energy profiles. The results show that the barrierless  $\beta$ -scission forming a vdW complex to produce OH-elimination production (RC1-2  $\rightarrow$  2MButene...OH  $\rightarrow$  2M1Butene + OH) with the barrier of 27.01 kcal/mol is great significant. As a long-chain alcohol, the barriers of the H transfer reactions (or isomerization reactions) of 2-methyl-1-butanol radials are lower. Thus the main decomposition pathways of other 2-methyl-1-butanol radicals (RC1-1, RC1-3, RC1-4, RC1-5 and RC1-6) are the CH<sub>2</sub>O-elimination reaction.

# Keywords

2-Methyl-1-butanol radicals, Decomposition, Isomerization, Potential energy surface.

# Introduction

The worldwide reduction of fossil fuels reserves in recent years has attracted the interests of researchers to put their attentions into renewable biofuels, such as bio-alcohols, bio-hydrogen, and biodiesel (Demirbas, 2007). Bio-alcohols as the "next generation" fuels have many potential properties, i.e. bio-alcohols are easier to be degraded by microorganism than fossil fuels, as alternative fuels the use of bio-alcohols in energy industry can reduce the emission of green-house gases (Demirbas, 2005, Demibas, 2008). Moreover, bio-alcohols can be obtained via microorganisms metabolic engineering based amino acid and lignocellulose, which can recover the biomass waste at the same time (Demirbas, 2007).

2-Methyl-1-butanol (2M1B), which is a isomer of pentanol, has higher energy density (28.38 kJ/cm3) than ethanol (21.11 kJ/cm3) and n-butanol (26.90 kJ/cm<sup>3</sup>), lower vapor pressure (0.4 kPa, 294.15 K) than ethanol (5.95 kPa, 294.15 K) and n-butanol (0.56 kPa, 294.15 K),(Li et al., 2013) lower water solubility and is easier mixed with hydrocarbons (Johnson and Goldsborough, 2009). The physical characteristics of 2-methy1-butanol are closer to real fuels. It is great significant to study the methods how to obtain 2-methyl-1-butanol and how to increase the production. Since the bio-synthesis of pentanol was realized, the strategies about the production of higher alcohols in metabolic engineering of microorganisms have been the hot spots for years (Choi et al., 2014). Recently, Su et al. (2015) used the hydrolysates of duckweed as fermentation substrates to produce higher alcohols including 2-methyl-1-butanol via biological

Compared with 1-pentanol and isopentanol (3methyl-1-butanol), the studies about 2-methyl-1butanol are limited. Recently, ignition delay time (Tang et al., 2013), laminar flame speeds (Li et al., 2013) and oxidation reactions of 2-methyl-1-butanol in jet-stirred reactor (Serinyel et al., 2014) were measured by many research groups. Zhang et al. (2015) developed a kinetic model of 2-methyl-1-butanol including 177 species and 994 reactions and validated the model using experimental dates that measured in the pyrolysis of reactant. Lucasse et al. (2015) investigated the combustion chemistry of 2-methyl-1-butanol in lowpressure premixed flames. And the proposed model based on previous studies of butanols and isopentanol showed good capabilities. In theory, Zhao et al. (2012) calculated the bond dissociation enthalpies (BDEs) of 1-pentanol, 3-methy-1-butanol and 2-methyl-1-butanol, and computed the temperature- and pressure-rate constants of some dominant channels. In order to further understand the combustion characteristics of 2methyl-1-butanol and develop detail kinetic model with better capabilities, more accurate kinetic data are desired.

The 2M1B radicals formed via unimolecular decomposition and H-abstraction reactions of 2-methyl-1-butanol is significant in combustion chemistry. The structures of these radicals (RC1-1 to RC1-6) are shown in Figure 1. In our present work, the dominant decomposition and radical isomerization pathways of 2M1B radicals were investigated by CBS-QB3 and QCISD(T)/CBS//M062x/cc-pvtz methods. The major isomerization and decomposition reactions

metabolism of *Corynebacterium crenatum*. Although the mass production of higher alcohols has not been achieved until now, the works are fundament for further studies.

Corresponding authors. E-mail: zld@ustc.edu.cn

channels were discussed based on the potential energy profiles.

# **Theoretical Methods**

The reaction pathways of 2M1B radicals were calculated by CBS-QB3 and QCISD(T)/CBS//M062x/cc-pvtz methods. For the QCISD(T)/CBS//M062x/cc-pvtz method, the geometry optimization and vibrational frequencies were computed by M062x method with the cc-pvtz basis set. Zero-point energy (ZEP) corrections were also obtained from the M062x//cc-pvtz calculation. The high level stationary point energy on the PESs were obtained from a scheme (expression (1)) (Zhang et al., 2013, Zhang et al., 2015) which is more computationally efficient than the normal restricted QCISD(T) (quadratic configuration interaction with singles doubles and perturbative inclusion of triples) calculation. In this work, all the calculations were performed with Gaussian 09 program package (Frisch et al., 2009).

 $E[QCISD(T)/CBS] = E[QCISD(T)/cc-pvtz] \times 1.4629 E[QCISD(T)/cc-pvdz] \times 0.4629 + E[MP2/cc-pvqz] \times 1.6938$   $- E[MP2/cc-pvtz] \times 2.1567 + E[MP2/cc-pvdz] \times 0.4629$ (1)

# **Results and Discussion**

Figure1 shows the optimized geometries of 2M1B radicals at M062X/cc-pvtz level. The calculated reaction channels at CBS-QB3 level were shown in Figures 2-6. The main reaction channels were also calculated at QCISD(T)/CBS//M062X/cc-pvtz level and were shown in Figures 7-9. The energies in the brackets were calculated by CBS-QB3, and without brackets were calculated by QCISD(T)/CBS//M062x/cc-pvtz method.



Figure 1. Optimized geometries of 2M1B radicals at M062x/cc-pvtz level.



Figure 2. The calculated PESs for isomerization pathways of six 2M1B radicals at CBS-QB3 level (unit:kcal/mol).





Figure 4. The calculated PESs for  $\beta$ -scission pathways of RC1-2 (unit:kcal/mol).



Figure 5. The calculated PESs for  $\beta$ -scission pathways of RC1-3 and RC1-4 (unit:kcal/mol).



Figure 6. The calculated PESs for  $\beta$ -scission pathways of RC1-5 and RC1-6 (unit:kcal/mol).



Figure 7. The calculated PESs for major isomerization pathways of six 2M1B radicals (unit:kcal/mol).



Figure 8. The calculated PESs for major unimolecular decomposition pathways of RC1-1, RC1-3, RC1-4, RC1-5 and RC1-6(unit:kcal/mol).



Figure 9. The calculated PESs for major unimolecular decomposition pathways of RC1-2 (unit:kcal/mol).

For the reactions of RC1-2, the transition state of the  $\beta$ -C-O scission cannot be evaluated at CBS-OB3 level and the transition state (TS12) relates to the 1, 2-OH transfer. The M062X/cc-pvtz calculations give the transition state (TS13) and the complex (2M1Butene...OH). It's worth noting that the channel (solid line shown in Figure 9) of RC1-2 directly decomposition reaction to produce bimolecular productions (2M1Butene + OH) through a van der Waals (vdW) complex (2MButene...OH) can't be neglected, which has been proved to be significant in the decomposition reactions  $\beta$  alcohol radials (Zhang et al.).That is consistent with previous study. Thus in this work, the main discussion is based on the QCISD(T)/CBS//M062x/cc-pvtz results.

Figure 7 displays the main isomerization channels among the six 2M1B radicals. The H transfer reaction between RC1-5 and RC1-6 is easier than other isomerization reactions, i.e. the barrier height of TS6 is 18.94 kcal/mol, which is 15.42 kcal/mol lower than that of TS2. The main reason is that the H transfer between RC1-5 and RC1-6 via six-member ring transition state has pretty low barrier value. The RC1-1, RC1-3 and RC1-4 can also isomer to RC1-6 with the barriers of less 30 kcal/mol, whereas the barriers of RC1-2 isomer to other radicals are relative higher (> 34 kcal/mol at QCISD(T)/CBS level).

In the combustion chemistry of 2M1B, followed the H-abstraction,  $\beta$ -scission may be the most competitive channels. The barrier heights of these channels are all less than 35 kcal/mol. The barriers of the main  $\beta$ -scission of RC1-1, RC1-3, RC1-4, RC1-5 and RC1-6 are 29.44, 32.39, 30.95, 33.65 and 21.67

kcal/mol, respectively. At the same time, the overall barriers of RC1-1 isomers to RC1-5 and RC1-3, RC1-4, RC1-5 isomer to RC1-6 are 25.96, 29.56, 26.29, 18.94 kcal/mol, respectively, which are low too Thus, the radical decomposition to CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>3</sub> + CH<sub>2</sub>O may be the main channel for the RC1-1, RC1-3, RC1-4, RC1-5 and RC1-6 from the PESs. On the other hand, we need to pay attention that almost all the barriers of RC1-2 decomposition reactions are pretty low, i.e. the value of TS13 is 27.01 kcal/mol, 2.43 - 6.64 kcal/mol lower than transition states in the  $\beta$ -scission of the other radicals except for RC1-6. And the barriers of isomerization reactions of RC1-2 are higher. Thus the main bimolecular products of RC1-2 are OH and 2M1Butene.

#### Conclusion

As a potential biofuel, the studies of 2-methyl-1-butanol in combustion chemistry are great significant. There are more and more research groups focus on this long-chain alcohol. In this study, the CBS-QB3 and QCISD(T)/CBS//M062x/cc-pvtz methods were used to investigate the isomerization and decomposition pathways of 2M1B radicals. The PESs of these channels and potential energy profiles are obtained, and the competitive reactions were discussed.

The dominant reaction channels include RC1-1, RC1-3, RC1-4 and RC1-5 isomer to RC1-6 and the  $\beta$ -scission of RC1-6 (RC1-6  $\rightarrow$  CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>3</sub> + CH<sub>2</sub>O). So CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>3</sub> and CH<sub>2</sub>O are major decomposition products of 2M1B radicals. Considering the decomposition reactions of RC1-2, the barrierless  $\beta$ -C-O-scission forming a vdW complex to produce bimolecular productions (RC1-2  $\rightarrow$  2MButene...OH  $\rightarrow$ 2M1Butene + OH) can't be ignored. In order to further validate our conclusion, the kinetic dates will be calculated in the following works. And our works will provide more useful dates for the construction of submechanism of 2M1B combustion.

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# MODELLING APPROACHES FOR THE COMBUSTION OF COKE DEPOSITED ON CRACKING CATALYSTS

Aitor Ochoa, Idoia Hita<sup>\*</sup>, Álvaro Ibarra, Maite Artetxe, José María Arandes, Pedro Castaño Department of Chemical Engineering. University of the Basque Country (UPV/EHU). P.O. Box: 644, 48080. Bilbao-Spain

Keywords: Coke deactivation, regeneration, catalytic cracking catalyst, MFI or HZSM-5 zeolite, FAU or HY zeolite

- Zeolites are widely used catalysts for the sustainable production of fuels and chemicals using renewable and waste materials, as well as for the conversion of fossil vacuum gasoil (VGO) within the most intensive catalytic transformation of the actual refinery scheme; the fluid catalytic cracking (FCC) unit. Zeolites are commonly deactivated by coke deposition and in this regard temperature programmed oxidation (TPO) is useful for gaining insights into the amount, composition, location or regeneration of coke.<sup>1</sup> In this work, we have compared several methods for obtaining kinetic data of the combustion of coke using (i) one or more kinetic expressions, (ii) isoconversional (model-free) methods and (iii) modulated (model-free) methods. We have applied these approaches to the combustion of 2 agglomerated zeolite extrudate systems that are representative of 2 crucial cracking paradigms: (i) HZSM-5 zeolite-based catalyst employed in a sequential pyrolysis-catalytic cracking of polyethylene waste and (ii) HY zeolite-based catalyst employed in the cracking of VGO, bio-oil (produced by the pyrolysis of biomass) and a VGO/bio-oil blend.
- The complete protocols of catalyst preparation, properties and reaction-analysis can be found elsewhere.<sup>2</sup> The coke combustion runs were performed in a TGA Q5000TA following the sequential steps of different heating ( $\beta$ ) rates of 1-20 °C min<sup>-1</sup> and/or modulation; amplitude (A) and frequency ( $\omega$ ).
- Assuming independent combustion models, both activation energy and frequency factor values increased as the heating rate increased, as a result of the parallel coke ageing<sup>3</sup> with the combustion. However, heating rates higher than 15 °C min<sup>-1</sup> lead to diffusional limitations within the catalyst fines. Isoconversional model-free methods are powerful tools since they assume different performance for each combustion fraction ( $\alpha$ ), although they require a higher amount of experiments. Modulated



Fig. 1. Activation energy obtained by modulated method using different parameters, for the deactivated catalyst used in the pyrolysis-cracking of HDPE.

model-free methods allow obtaining kinetic constants within one single experiment; however, those constants are a function of the temperature ramp parameters ( $\beta$ , A and  $\omega$  as shown in Fig. 1). In this work we report the protocols for obtaining the intrinsic combustion constants with modulated methods.

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# FROM RICH TO LEAN CONDITIONS, DIMETHOXYMETHANE OXIDATION MODELING AT HIGH PRESSURES

L. Marrodán\*, Á. Millera, R. Bilbao and M.U. Alzueta

Aragón Institute of Engineering Research (I3A). Department of Chemical and Environmental Engineering. University of Zaragoza. 50018 Zaragoza. Spain

### Abstract

The use of dimethoxymethane (DMM, CH<sub>3</sub>OCH<sub>2</sub>OCH<sub>3</sub>) in diesel engines has received more and more attention because of its high oxygen content and therefore its potential to reduce soot emissions. A deep study of its oxidation has been carried out from both experimental and modeling points of view. It was first initiated with a DMM oxidation work at atmospheric pressure. The next step, addressed in this work, consists of an experimental study of DMM conversion at high pressures (20-60 bar), covering a large range of temperatures from fuel rich to fuel lean conditions, together with the validation of a kinetic mechanism taken from the previous work and modified in the present work to account for the high-pressure conditions.

The results indicate that the main consumption of DMM occurs through H abstraction reactions to form  $CH_3OCH_2OCH_2$  and  $CH_3OCHOCH_3$  radicals. Under the conditions studied in this work,  $O_2$  and  $HO_2$  radicals could play an important role, and, although their reactions with the DMM radicals were omitted in the Dias et al. submechanism, they have been included in our present final mechanism since they appear to be significant. Another important aspect is related to the pathways involving peroxy species, especially  $CH_3OCH_2O_2$ , which seem to be important under the high-pressure conditions.

# Keywords

Oxidation, Dimethoxymethane, Modeling, High-pressure.

#### Introduction

The high fuel efficiency is one of the major advantages of diesel engines. However, they highly contribute to nitrogen oxides (NO<sub>x</sub>) and particulate matter (mainly soot) emissions. Because of the trade-off between both of them (NO<sub>x</sub> formation is favored under fuel lean conditions, and soot is formed when oxygen is in default), reducing simultaneously both emissions is really difficult. This still remains as one of the major challenges in diesel engines development due to the increasing concern on environmental protection.

Reformulation of diesel fuels by the addition of oxygenated compounds can effectively reduce this kind of emissions (Yanfeng et al., 2007). Dimethoxymethane (DMM, CH<sub>3</sub>OCH<sub>2</sub>OCH<sub>3</sub>), with its high oxygen fraction, relative high cetane number, high volatility and good solubility with diesel fuels is a diether considered to be a potential fuel additive. Several studies have analyzed the effect of adding DMM to base diesel on emissions of compression ignition engines (e.g. Huang et al., 2006) or direct injection (e.g. Ren et al., 2006) and, in general, diesel-DMM blends increase engine performance and decrease exhaust pollutant emissions. • To whom all correspondence should be addressed (marrodan@unizar.es)

However, few studies have been focused on the combustion characteristics of pure DMM at high temperatures and pressures. Daly et al. (2001) studied, in a jet stirred reactor, the oxidation of DMM at 5 bar, high temperatures 800-1200 K and different equivalence ratios (0.444, 0.889 and 1.778) and they proposed a submechanism containing 50 reactions to describe the DMM conversion. Afterwards, Dias et al. (2010) built a new mechanism containing 480 reactions, by using kinetic data taken from the literature, mainly from Daly et al. (2001), in order to simulate the DMM flames.

In this context, it is worthwhile to mention a previous work of our research group about the DMM oxidation at atmospheric pressure, from pyrolysis to high-oxidizing conditions, from both experimental and modeling points of view (Marrodán et al., 2015). The final mechanism compiled in that work has been taken as the initial mechanism in the present work.

# Experimental

Experiments have been carried out in an experimental installation previously used by our research group with success. A complete description can be found in Marrodán et al. (2014). Specifically, experiments have been performed under well-

controlled flow reactor conditions, in the 373-1073 K temperature range, for different pressures (20, 40 and 60 bar), and the oxygen concentration was varied from 1960 to 56000 ppm, that is from fuel rich ( $\lambda$ =0.7) to fuel lean conditions ( $\lambda$ =20), being  $\lambda$  the air excess ratio.

### Modeling

The experimental results have been analyzed in terms of a detailed gas-phase chemical kinetic mechanism for describing the DMM oxidation. The model that has been used as starting point was the one compiled by Marrodán et al. (2015) in the previously appointed DMM atmospheric oxidation work. This latter mechanism was built by adding different reaction subsets found in the literature to the model developed by Glarborg et al. (1998) updated and extended later (Glarborg et al., 2003 and Skjøth-Rasmussen et al., 2004). Additional subsets for the different involved compounds were added: dimethyl ether (DME) (Alzueta et al., 1999), ethanol (Alzueta and Hernández, 2002), acetylene (Alzueta et al., 2008), and methyl formate (Marrodán et al., 2014). Thermodynamic data for the involved species were taken from the same sources.

The resultant mechanism validated with the experimental results (from now on, initial mechanism), has been modified in the present work to account also for the high-pressure conditions studied in the DMM oxidation. The changes made will be described below.

Reaction with hydroxyl radicals (OH) is an important step in the oxidation of organic compounds in combustion systems (Arif et al., 1997). The main consumption of DMM occurs through H abstraction reactions by OH to form  $CH_3OCH_2OCH_2$  and  $CH_3OCHOCH_3$  radicals (reactions 1 and 2). The kinetic parameters of these reactions have been modified from the initial mechanism.

 $CH_{3}OCH_{2}OCH_{3} + OH \rightleftharpoons CH_{3}OCH_{2}OCH_{2} + H_{2}O$ (1)

$$CH_{3}OCH_{2}OCH_{3} + OH \rightleftharpoons CH_{3}OCHOCH_{3} + H_{2}O$$
(2)

In the Dias et al. (2010) DMM reaction subset, the rate constant of these reactions is estimated by analogy with the reaction  $CH_3OCH_3 + OH = CH_3OCH_2 + H_2O$  from DeMore and Bayes (1999), with a proposed value of  $9.10 \cdot 10^{12}$  exp(-496/T) cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, determined experimentally in the 263-361 K temperature range. Arif et al. (1997) determined a rate constant of  $6.32 \cdot 10^6$  T<sup>2</sup> exp(327/T) cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, in the 295-650 K temperature range, which is adopted in this study, also used in the work of Alzueta et al. (1999) and that is in agreement with the high-temperature (923-1423 K) determination of Cook et al. (2009). With this value, the latest authors achieved a good fit for both the low and the high temperature measurements.

The prevalence of  $HO_2$  radicals under high pressure, and preferably lean conditions, should make them to play an important role under the conditions of the present work. Reactions involving DMM and  $HO_2$  radicals (reactions 3 and 4) were not included in the initial reaction mechanism and we have included them in the present work.

 $CH_{3}OCH_{2}OCH_{3} + HO_{2} \rightleftharpoons CH_{3}OCH_{2}OCH_{2} + H_{2}O_{2}$ (3)

$$CH_3OCH_2OCH_3 + HO_2 \rightleftharpoons CH_3OCHOCH_3 + H_2O_2$$
(4)

The rate constants for reactions 3 and 4 have not been directly measured to our knowledge and, therefore, there is some degree of uncertainty in their absolute values. For reaction 3, the rate parameters have been taken by analogy of the dimethyl ether and HO2 reaction, following the same procedure described by Daly et al. (2001), and likewise taking the value,  $1.00 \cdot 10^{13} \exp(-8900/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , from the work of Curran et al. (1998). The rate constant for abstraction of a secondary hydrogen atom (reaction 4) was estimated by Daly et al. (2001) from the value for reaction 3, with the A factor divided by a factor of 6. These authors stated that DMM has six primary hydrogen atoms and only two secondary ones, so the probability of attack will therefore be lower for the attack on the CH<sub>2</sub> groups than on the CH<sub>3</sub> groups. Also, the proximity of two oxygen atoms to the central carbon atom of the molecule will make the hydrogen atoms attached to it more labile than those belonging to the methyl groups. As a result, the activation energy for reaction 4 should be lower than for reaction 3. Thus, a rate constant value of  $2.00 \cdot 10^{12} \exp(-7698/T) \text{ cm}^3 \text{ mol}^{-1}$ s<sup>-1</sup> was proposed by Daly et al. (2001) for reaction 4, which is adopted in the present mechanism.

Although the reactions of CH<sub>3</sub>OCH<sub>2</sub>OCH<sub>2</sub> and CH<sub>3</sub>OCHOCH<sub>3</sub> radicals with O<sub>2</sub> (reactions 5 and 6) and HO<sub>2</sub> (reactions 7 and 8) were omitted in previous DMM mechanisms (Curran et al., 1998, Dias et al., 2010, Marrodán et al., 2015), they can play an important role in the oxidation of DMM, particularly under high-pressure and high-oxygen-concentration conditions and, therefore, these reactions have been included in our final mechanism.

 $CH_3OCH_2OCH_2 + O_2 \rightleftharpoons CH_2O + CH_3OCHO + OH$  (5)

 $CH_{3}OCHOCH_{3} + O_{2} \rightleftharpoons CH_{2}O + CH_{3}OCHO + OH$ (6)

 $CH_{3}OCH_{2}OCH_{2} + HO_{2} \rightleftharpoons CH_{2}O + CH_{3}OCH_{2}O + OH$ (7)

 $CH_3OCHOCH_3 + HO_2 \rightleftharpoons CH_3OCHO + CH_3O + OH$  (8)

For reactions 5 and 6, the rate constants have been estimated establishing an analogy with the reaction of methoxy-methyl radical (CH<sub>3</sub>OCH<sub>2</sub>, generated in the dimethyl ether thermal decomposition) and oxygen molecular, as previously done by Daly et al. (2001). In that case, they chose the kinetic parameters given by Dagaut et al. (1996); namely,  $1.70 \cdot 10^{10}$  exp(337/T) cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, which were estimated based on C<sub>2</sub>H<sub>5</sub> + O<sub>2</sub> kinetics. However, here, we have chosen a value of the CH<sub>3</sub>OCH<sub>2</sub> + O<sub>2</sub> rate constant of  $2.50 \cdot 10^{11}$  exp(850/T) cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, obtained by Alzueta et al. (1999) from averaging three room-temperature determinations (Hoyermann and Nacke, 1996, Sehested et al., 1996, Sehested et al., 1997), and adopting the temperature dependence reported in Hoyermann and Nacke (1996), which is significantly faster than that proposed in the mechanism of Dagaut et al. (1996).

The analogy with reactions  $CH_3OCH_2 + HO_2$  has been applied to obtain the rate constants of reactions 7 and 8. Not much information has been found related to these reactions, and the value proposed by Daly et al. (2001), based on estimations made by Dagaut et al. (1996), has been chosen. This value is, for reaction 7,  $3.00 \cdot 10^{11}$ cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, and for reaction 8 they increased this value to  $1.00 \cdot 10^{12}$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>.

Curran et al. (1998) stated that the pathway involving peroxy intermediates may be important at low temperatures (below approximately 900 K) and pressures higher than 10 bar, because the bimolecular addition of methoxy-methyl radical to  $O_2$  has a lower activation energy barrier than the  $\beta$ -scission to yield CH<sub>2</sub>O and CH<sub>3</sub>, the two main pathways that methoxymethyl radicals can undergo. At atmospheric pressure, the formation of methoxy methyl-peroxy intermediate is not predicted to be significant, except for a minor contribution for very lean stoichiometries (e.g. Alzueta et al., 1999).

At high pressures (20, 40 and 60 bar) and fuel lean conditions, the reactions forming peroxy species (reactions 9 and 10) may have an important impact on the oxidation chemistry of DMM and, therefore, these reactions have been included in our final mechanism.

 $CH_{3}OCH_{2}OCH_{2} + O_{2} \rightleftharpoons CH_{3}OCH_{2}O_{2} + CH_{2}O$ (9)

#### $CH_{3}OCH_{2}OCH_{2} + HO_{2} \rightleftharpoons CH_{3}OCH_{2}O_{2} + CH_{2}OH$ (10)

For reaction 9, the kinetic parameters have been estimated by analogy with the reaction of methoxy-methyl radical with molecular oxygen. The  $6.40 \cdot 10^{12} \exp(-45.80/\text{T}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  value for CH<sub>3</sub>OCH<sub>2</sub> + O<sub>2</sub> was considered in an earlier mechanism by our group (Alzueta et al., 1999). For reaction 10, no values of kinetic parameters were found, and we have considered initially a reaction rate of  $1.0 \cdot 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The results of sensitivity analysis, shown later, indicate no significant impact of this estimation.

Model calculations have been performed using both SENKIN (Lutz et al., 1988) from the CHEMKIN II (Kee et al., 1991) software package and CHEMKIN-PRO (2013), considering pressure constant in the reaction zone and the corresponding temperature profile.

# Results

The experimental results have been analyzed in terms of the kinetic mechanism proposed in the present work. Figure 1 shows a comparison between the experimental results (symbols) and the modeling results (lines) obtained for rich conditions ( $\lambda$ =0.7) and different pressures in the DMM oxidation. The suggested model predicts the general trend of the DMM concentration profile for the different pressures studied. As can be seen, working at 20, 40 or 60 bar does not have an effect on the oxidation of DMM.



Figure 1. Influence of pressure on DMM concentration as a function of temperature for fuel rich conditions  $(\lambda=0.7)$ .

In the same way, Figure 2 shows the experimental and modeling results obtained, in this case, for fuel lean conditions ( $\lambda$ =20). The introduction in the mechanism of the different reactions, especially those forming peroxy species (reactions 9 and 10), has allowed the model to predict the experimental constant DMM concentration zone found at approximately 598 K, which appears to be associated to the oxygenated CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub> species.



Figure 2. Influence of pressure on DMM concentration as a function of temperature for fuel lean conditions  $(\lambda=20)$ .

# Conclusions

An experimental and modeling study of the DMM oxidation covering a wide range of temperatures (373-1073 K), and pressures (20, 40 and 60 bar), from fuel rich to fuel lean conditions, has been carried out.

Experimental results and model calculations are, in general, in good agreement, and the main trends in the concentration profiles are well predicted for the theoretical model.

Working at 20, 40 or 60 bar, does not have a big influence on the DMM oxidation.

Under fuel lean conditions, the DMM conversion is fast until approximately 598 K, where the concentration of DMM presents a plateau and remains constant. This zone appears to be associated to the formation of the intermediate CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub> oxygenated species. The addition of some reactions involving these species to the mechanism has allowed a better agreement between experimental data and model calculations.

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# INVESTIGATIONS ON THE CATALYTIC EFFECTS OF POTASSIUM AND SILICON IN THE THERMO-CHEMICAL GASIFICATION OF AGRICULTURAL RESIDUES

Hofmann A.<sup>\*1,2)</sup>, Huemer M.<sup>1)</sup>, Bozic D.<sup>1)</sup> and Huber, M.B.<sup>1)</sup>

MCI – Department for Energy Engineering, Maximilianstraße 2, A-6020 Innsbruck, Austria
 Technical University of Vienna, Getreidemarkt 9, A-1040 Vienna, Austria

#### Abstract

The gasification of agricultural residues, e.g. of wheat straw, shows a high potential for the contribution to renewable energy systems. The high amount of alkali salts in straw causes low ash melting temperatures - sintering effects in the gasification reactor are the consequence. Potassium shows also the potential to support the gasification reactions. Therefore, with potassium-rich biomass, high carbon conversion ratios can be reached at lower temperatures than with conventional gasification. The investigations of this study are focusing on the quantification of the catalytic effects of the ash components potassium and silicon on the reaction kinetics of gasification to find the optimum gasification conditions avoiding sintering effects on the one hand and realizing efficient carbon degradation on the other hand.

# Keywords

Heterogeneous kinetics, gasification reactions, Boudouard reaction, biomass gasification, catalytic effects of Potassium and Silicon

#### Introduction

The gasification of agricultural residues, mainly of crop straw, shows a high potential for the contribution to renewable energy systems. Nevertheless, the high amount of alkali salts in the feedstock causes low ash melting temperatures (Rathbauer, Thrän, Kaltschmitt, 2001). Sintering effects in the gasification reactor are the consequence. Other problems are the release of alkali metals and chlorine emissions with high gasification temperatures (Bläsing, Zini, Müller, 2012). For this reasons, many research groups focus on possibilities to raise the ash melting temperatures of the biomass by additives (e.g. Wang et.al, 2010 and Mann et.al, 2010) or investigate on high-temperature gasification processes to reach a controlled liquid ash flow described by Kleinhappl et.al (2010).

Nevertheless, potassium shows also the potential to support the gasification reactions (Koenig, Squires, Lauerendeau, 1986). Therefore, with potassium-rich biomass, high carbon conversion ratios can be reached at lower temperatures than with conventional gasification, described by Hattingh et.al. (2011). The investigations of this study are focusing on the quantification of the catalytic effects of potassium and other ash components on the gasification reaction kinetics (Umeki et. al, 2012) of agricultural biomass to find the optimum gasification conditions avoiding sintering effects on the one hand and realizing efficient carbon degradation on the other hand.

This could be realized with a new approach in gasification technology: a multi-staged gasification system basing on the floating bed reduction (FBR) technology introduced by Huber et.al (2013). This technology allows the control of the gasification parameters in the different gasification stages; especially the gasification temperature can be controlled by separate air inlets in each zone. The FBR-process is designed as an auto-thermic process whereby air is used as a gasification agent. The gasification process consists of four principal processes: drying (up to 200°C), pyrolysis (up to 500°C), oxidation (up to 1,000°C) and reduction (700 – 900°C).

# **Gasification reactions**

The main object of gasification is the conversion of solid biomass into a hydrogen- and carbon monoxide- rich gas. Those components are built mainly in the reduction zone of the gasifier. Although the formation of the product gas is subjected also to homogeneous equilibrium reactions (cf. eq. (1), (2)), the main focus is set on the main heterogeneous carbon degradation reactions described in eq. (3), (4) because with the ongoing carbon degradation of the charcoal in the reduction reactor, the ash components are concentrated and will lead to sintering effects on the char surface (Hofmann, Huemer, Huber 2014).

$CH_4 + H_2O \leftrightarrow CO + 3 H_2$	$\Delta H = +203,0 \ kJ/mol$	(1)
$CO_2 + H_2 \leftrightarrow CO + H_2O$	$\Delta H = + 40,9 \ kJ/mol$	(2)
$C_{(s)} + CO_2 \leftrightarrow 2 CO$	$\Delta H = +118,5 \ kJ/mol$	(3)
$C_{(s)} + H_2 0 \leftrightarrow C 0 + H_2$	$\Delta H = +159,9  kJ/mol$	(4)

For the investigations in this work, the Boudouard-reaction (3) was selected as a model

reaction due to its main contribution on autothermic gasification processes (Hofbauer, 2007).

#### **Concept and Methodology**

#### General gasification behavior of different biomass

The elementary composition of different biomass (spruce, wheat- and spelt straw) was analysed to identify the composition of the inorganic components.

The different biomass samples have been pyrolysed in a lab-scale pyrolysis reactor at 550°C under nitrogen atmosphere, whereby the hydrogen and oxygen in the biomass is converted fully into pyrolysis gas so that the remaining charcoal consists only of carbon and the mineral components.

The gasification behavior of the pyrolysed biomass has been investigated by means of thermogravimetric analyses (Mettler Toledo TGA/DSC1, STAR<sup>e</sup> System) with CO<sub>2</sub> as an active gas to simulate the Boudouard reaction. There was a significant stoichiometric surplus of CO<sub>2</sub> chosen (min. 50:1) to shift the equilibrium in the direction of maximum carbon degradation and to lower the influence of the diffusion effects of the different samples.

For the principal classification of the different biomass types, a dynamic gasification program was chosen to describe the carbon degradation ratio  $X_C$  as a function of temperature in a range between 500°C and 1,100°C (see Table 1).

*Table 1. TGA-method for dynamic gasification*  $X_C(T)$ 

Duration	Temp.	Heat rate	Gas
9.5 min	25 500°C	50 K/min	N2, 60 ml/min
120 min	500 1,100°C	5 K/min	CO2, 80 ml/min

The carbon degradation ratio  $X_C$ , related on the carbon content of the pyrolysed biomass, is described by eq. (5):

$$X_C = \frac{[C] t = x}{[C] t = 0}$$
(5)

Influence of potassium and silicon on the gasification behavior

To measure the influence of the inorganic components on the reaction kinetics, the method of standard addition of potassium (as  $K_2CO_3$ ) and silicon (as SiO<sub>2</sub>) to spruce char as a reference biomass was used to produce the samples for the TGA-tests. The added concentrations were selected in a range of 0.5 and 5.0 mass% of [K] and [Si], related on the carbon content of the pyrolysed spruce char.

To describe the catalytic/inhibiting effects of the additives, the reaction rate of the carbon degradation was analyzed by means of an isothermal TGA-method (see Table 2) at temperatures of 750°C, 850°C and 950°C.

Table 2. TGA-method for isothermal gasification  $X_C(t)$ 

Duration	Temp.	Heat rate	Gas
dynamic	25°C T <sub>iso</sub>	50 K/min	N2, 60 ml/min
2 min	Tiso	0 K/min	N2, 60 ml/min
15 min	Tiso	0 K/min	CO2, 80 ml/min

For the calculation of the reaction ratio (eq. 6), the slope of the regression line of the mass loss of the isothermal TGA-curves was selected. The calculation interval was chosen in the most linear segment of the curve (evaluated by first derivation analyses) and was standardized for all analyses with 300 seconds, starting after 360 seconds of the isothermal interval. To regard the diffusion effects of the sample, the carbon degradation speed is also related to the sample volume  $V_s$ . Therefore, the reaction rate  $r_c$  can only serve as a relation between two samples, treated by the same procedure.

$$r_{C} = \frac{[C] (t = 660s) - [C] (t = 360 s)}{V_{s} * 300 s} [mol/l * s]$$
(6)

# Results

Gasification behavior of different biomass

Table 3 shows the elementary analyses of the different analysed biomass samples.

[mg/kg <sub>dm</sub> ]	Spruce chips	Wheat straw	Spelt straw
Carbon	504,400	475,400	456,500
Hydrogen	61,000	58,900	58,700
Oxygen	429,000	419,000	413,000
C:H:O-ratio	1:1.45:0.64	1:1.49:0.66	1:1.54:0.68
Potassium	347	10,500	5,820
Silicon	64	6,180	17,100
K:Si (mass)	1:0.18	1:0.59	1:2.9
K:Si (mole)	1:0.26	1:0.82	1:4.1

Table 3. Elementary composition of biomasses

In comparison with spruce, both straw samples show significant higher concentrations of potassium and silicon, whereby the K:Si-ratio is higher with wheat straw than with spelt straw.

Figure 1 shows the gasification behavior described as carbon degradation as a function of temperature of the three selected biomasses.



Figure 1. Gasification behavior of biomasses

The carbon degradation ratios of the three samples do not vary significantly with temperatures lower than 750°C. Starting at about 800°C, the sample with the higher K:Si-ratio shows faster carbon degradation than the sample with the lower K:Si-ratio.

#### Influence of potassium and silicon

Figure 2 shows the influence of the potassium concentration on the reaction rate at different temperatures. The concentration "0%" represents the spruce sample without additives.



Figure 2. Influence of potassium on reaction rate

At 750°C, the influence of the potassium concentration is not significant. With increasing temperature and potassium content, a clear increase of the reaction speed can be observed whereby the highest slope can be observed in the concentration range of between 0.5 and 1.0 mass%.

Figure 3 shows the influence of the silicon concentration at different temperatures.



Also in this case, no significant influence at 750°C can be shown. In comparison to the influence of potassium, silicon shows a contrary effect. There is a slight decrease of reaction speed with increasing concentration and temperature.

#### Discussion

The tested biomass samples show different compositions of the organic matter as well as of the inorganic components. Comparing the C:H:O-ratios of the biomass samples with the C:H:O-ratios of cellulose resp. hemi-cellulose (1:2:1) and of lignin (1:1.2:0.3), the amount of sugar-based molecules is higher than the amount of lignin, which is also described by Kravanja and Friedl (2010). Those molecules show different behavior in the first step of gasification, the pyrolysis. While cellulose and hemi-cellulose show a degradation ratio of >90% at 500°C, lignin is decomposed only at about 50% (Hellwig 1998). For this, the more celluloses a biomass contents, the more reactive is the biomass during gasification process. The degradation curve of wheat straw could be caused by this circumstance. But comparing the C:H:O-ratio of spelt straw, also this biomass show a higher amount of celluloses than of lignin compared with spruce, but the TGA-curve show a slower gasification behavior. For this, the gasification behavior cannot depend only on the organic composition.

Considering the effects of potassium on the gasification reactions (Umeki et. al, 2012) and the composition of the inorganic components of the tested biomass samples, the potassium-to-silicon-ratio is from special interest. The interaction between those ash constituents is described by Visser (2004): Silicon and potassium are able to build silicates in hightemperature-atmosphere an in presence of charcoal. With this, a part of the minerals could be de-activated and the dominant element could be responsible for the catalytic (potassium) or even an inhibiting (silicon) effect on the gasification reactions, which corresponds to the measured gasification behaviors of the both straw samples.

To describe the principal influence of potassium and silicon on the gasification behavior, spruce char was added with different concentrations of both elements. The results show a clear increase of the reaction rate with an increasing concentration of potassium and the opposite effect with increasing silicon content. Both effects are not significant at temperatures of 750°C but became more intensive with increasing temperature.

Transferring these results on the gasification in the floating bed reactor, the temperature in the oxidation zone could be reduced due to the higher reactivity of wheat straw to reach the same carbon conversion ratio than with spruce. Under laboratory conditions, a carbon conversion ratio of 80% is reached at 970°C with spruce and at 905°C with wheat straw (Fig. 4).



Figure 4. Temperature difference for  $X_C=0.80$ 

The standard gasification temperature for spruce with the FBR-technology is at about 850°C, whereby due to the high residence time of the char particles (several hours) a carbon conversion ratio of more than 90% is reached (Huber 2013). Sintering effects of wheat straw are described at temperatures beginning with about 850°C (e.g. Osmann 1983), therefore the reduction of the gasification temperature could reduce sintering effects.

#### **Conclusion and Outlook**

The gasification of agricultural biomass with high amounts of potassium and silicon, is characterized by sintering effects in the gasifier due to the low ash melting temperature caused by potassium.

Due to the supporting effects of potassium on the gasification reactions, melting effects of biomass ash can be reduced by lowering the gasification temperature. The floating bed reduction technology shows a high potential for the gasification of biomass with low ash melting points due to the staged plant concept with clear defined process steps.

Essential for this approach is the potassium-tosilicon-ratio. With a surplus of potassium, the reactions are accelerated and the gasification temperature can be lowered to reach an adequate carbon conversion ratio.

In a next step, gasification test have to be executed on a pilot gasification plant to evaluate the findings of the laboratory results.

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# A SINGLE-PULSE SHOCK TUBE COUPLED WITH HIGH-REPETITION-RATE TIME-OF-FLIGHT MASS SPECTROMETRY AND GAS CHROMATOGRAPHY FOR HIGH-TEMPERATURE KINETICS STUDIES

P. Sela\*, M. Aghsaee, J. Birkmann, B. Shu, J. Herzler, M. Fikri, C. Schulz, O. Welz Institute for Combustion and Gas Dynamics – Reactive Fluids, University of Duisburg-Essen, 47048 Duisburg, Germany

#### Abstract

Shock tubes are powerful and established devices to study the kinetics and mechanisms of chemical reactions in the gas phase at high temperatures. Various techniques have been coupled with shock tubes for species measurements. Most of the optical techniques provide time resolution with high sensitivity and selectivity but can measure only few species. In contrast, end-product analysis by gas chromatography (GC) enables detection of multiple stable species, but cannot detect transient intermediates and lacks time resolution. Here we present a new setup of a single-pulse shock tube coupled with high-repetition-rate time-of-flight mass spectrometry (HRR-TOF-MS) and GC. This combined setup enables simultaneous time-resolved kinetics measurements of multiple species using HRR-TOF-MS and complementary end-product identification by GC after quenching of the reactions in the shock tube and therefore enables the investigation of complex reaction systems at high temperature. To validate this setup, we determined the rate coefficient for the thermal decomposition of cyclohexene at temperatures between 1000 and 1500 K and pressures ranging from 0.8 to 2.4 bar using both HRR-TOF-MS and GC. Moreover, we compared the experimental results with literature data for cyclohexene decomposition.

# Keywords

Kinetics, cyclohexene, shock tube, mass spectrometry, gas chromatography

# Introduction

Shock tubes are established tools to study the chemical kinetics of gas-phase reactions at high temperatures<sup>1-3</sup>. Their advantage is the quasi-instantaneous ( $< 1 \mu s$ ) heating of the test gas to high temperatures over wide ranges of temperature and pressure. In the present study, a shock tube was equipped with a high-repetition-rate time-of-flight mass spectrometer (HRR-TOF-MS) and a gas chromatograph with mass spectrometric (GC-MS) and flame ionization detector (FID). HRR-TOF-MS enables the quasi-simultaneous time-resolved detection of multiple species. In addition the use of GC allows accurate, sensitive end-product. For the use of a GC homogeneous conditions must prevail for several milliseconds followed by rapid quenching by rarefaction waves resulting in a sudden drop in temperature and pressure. In order to prevent reheating of the test gas, a dump-tank was used to trap the reflected shock and secondary waves and to run the shock tube in single-pulse mode.

Combining time-resolved kinetics measurements of multiple species by HRR-TOF-MS with endproduct analysis by GC combines the advantages of both techniques and is therefore a strong tool to study and understand the chemical kinetics of complex reaction systems at high temperature.

The aim of this work is to validate this setup using the extensively investigated decomposition of cyclohexene  $(C_6H_{10})$  as a test system<sup>4-7</sup>. The kinetics of decomposition of cyclohexene is well known and proceeds in a single elementary step via a retro Diels-Alder reaction (see R1) to form only the closed-shell products ethylene  $(C_2H_4)$  and 1,3-butadiene  $(C_4H_6)^6$ :

$$C_6H_{10} \rightarrow C_2H_4 + C_4H_6 \tag{R1}$$

The absence of radical products avoids secondary radical chemistry<sup>6</sup> and therefore makes the decomposition of cyclohexene a well-suited test system for the validation of our setup.

#### Experiment

The experiments were performed in a stainless-steel shock tube with a total length of 8.8 m and an inner diameter of 80 mm. The shock tube is divided in a 2.5 m driver section and a 6.3 m driven section, separated by an aluminum diaphragm. The driver tube length could be reduced with a movable piston up to 80 cm to adjust the time arrival time of the rarefaction waves at the probe volume in the driven section and hence optimize the cooling rate by the expansion fan. The shock tube was additionally equipped with a 50 l mixing vessel and a 350 l dump tank for single-pulse experiments.

<sup>\*</sup> Corresponding author: <a href="mailto:paul.sela@uni-due.de">paul.sela@uni-due.de</a>

Before each experiment the shock tube sections were evacuated to ~  $8 \times 10^{-4}$  mbar using a four stage rotary pump (Edwards dry star, Model QDP 80) combined with a mechanical booster pump (Edwards, EH 500A).

Either helium or H<sub>2</sub> was used as driver gas. The diaphragm burst pressure was measured with a manometer (Keller, Mano 2000), and the pressure  $p_1$  of the test gas in the driven section was determined using a capacitance manometer (Edwards, Trans 600 AB). To determine the shock wave velocity and to measure the post-shock pressure, a set of five piezoelectric pressure tranducers was used. Four pressure transducers (PCB 112A05) were placed at intervals of 150 mm from the end plate. The fifth pressure tranducer (PCB 112A05) was positioned at a distance of 20 mm from the end plate. All signals of the pressure tranducers were detected by an oscilloscope (PicoScope 5000, Pico Technology). The pressure  $p_5$  and the temperature  $T_5$  behind the reflected shock wave were computed from ideal shockwave equations<sup>2,8</sup> based on the initial pressure  $p_1$ , initial temperature  $T_1$  in the driven section and the velocity of the incident shock wave using a 1-D model. The driven section was interfaced to a HRR-TOF-MS through a conical nozzle (diameter  $60 \,\mu$ m) centered at the end plate. For GC sampling, a magnetic valve sitting at with a distance of 20 mm to the end plate was connected to a probe chamber assembled with the GC device. The valve was triggered using a delayed signal of the fifth pressure transducer so that the probe chamber was automatically filled with the products of the test gas behind the reflected shock wave after the gas had been quenched. Reaction times were derived from the pressure profiles.

The HRR-TOF-MS (Kaesdorf) can be operated at repetition rates of up to 150 kHz in either linear or reflectron mode. An electron impact ion source was used for ionization and the kinetic energy of the ionizing electrons can be varied between 5 and 85 eV.



Figure 1. Intensity-time profile of Ar. Mixture: 0.25%  $C_6H_{10}$ , 0.25% Ar and 0.25% Xe in Ne.  $T_5 = 1.373$  K,  $p_5 = 1.3$  bar.

In the present study, the repetition rate was set to 100 kHz, the TOF-MS was operated in the reflectron

mode, and an ionization of 45 eV was used. For postpocessing the raw data from the HRR-TOF-MS, a novel self-written MATLAb-based software was used to convert the raw data into intensity-time profiles by a summation of the peak area or into mass spectra by summing over a certain time interval. A typical time profile of the inert gas Ar used as internal standard is shown in Figure 1. The internal standard was used to correct all species intensities during the initial phase of the build-up of the gas expansion after the arrival of the shock wave.

Stable end products were quantified using a GC (Agilent 7890A and MSD 5975C). The GC instrument was equipped with a PLOT Q column for separation of lighter species (up to C<sub>4</sub>) connected to a flame ionization detector (FID) and a HP5-MS column for separation of heavier species connected to a quadrupole mass spectrometer (QMS), i.e., GC/MS. For each GC/MS experiment a sample of gas mixture was taken and analyzed immediately for pre-shocked conditions and a second sample was taken automatically after the test gas had been quenched. Concentrations of the parent molecule  $C_6H_{10}$ , the product  $C_4H_6$  and the rare gases were analyzed by GC/MS, and the products C<sub>2</sub>H<sub>4</sub> and C<sub>4</sub>H<sub>6</sub> were monitored using the FID. Based on the pre- and post-shock concentrations of the parent molecule and the fixed reaction time described above, the reaction rate coefficient for R1 was determined assuming first-order conditions.

Test mixtures containing equimolar concentrations of 0.1-2% of  $C_6H_{10}$ , Ar and Xe, respectively, in Ne as the bath gas were prepared in a mixing vessel with a volume of 50 l and were stirred for at least 12 hours prior to use. Ar and Xe were both used as internal standards in the HRR-TOF-MS experiments. The signals of the internal standards Ar and Xe were used to correct the variations in the sensitivity of the TOF which is caused by varying mass flows through the nozzle into the ion source as a consequence of the pressure variation in the test section after arrival of the shock wave (see Fig. 1). Further information about the HRR-TOF-MS setup and the data acquisition are given in references<sup>9,10</sup>.

# **Results and discussion**

In an ideal single-pulse experiment, stable temperature and pressure conditions persist behind the reflected shock wave until the arrival of rarefaction waves rapidly cools the test gas. When using the combination of He as the driver gas and Ne as the bath gas, however, the interaction of the reflected shock wave with the contact surface (test gas / driver gas) leads to a secondary compression wave travelling towards the end plate and results in an additional heating of the test gas. This additonal heating introduces non-stationary shock conditions and therefore should be avoided. The reduction of the lenght of the driver section leads to an earlier arrival of the rarefaction waves in the test section and thus compensates for this heating by the compression wave. The effect of the driver section length is shown in Figure 2. A reduction by 60 cm at an initial post-reflected-shock temperature ( $T_5$ ) of 1490 K and 1.5 bar leads to an ideal pressure profile, in which additional heating of the test gas was suppressed in contrast to experiments with the original driver length.

The thermal decomposition of  $C_6H_{10}$  via R1 was investigated at  $T_5$  between 1000 and 1500 K and  $p_5$  between 0.8 and 2.4 bar. For comparison, two mass spectra from the HRR-TOF-MS experiment are shown in Figure 3. The top spectrum represents pre-shock conditions integrated for 0.6 ms before the arrival of the incident shock at  $T_1 = 295$  K and  $p_1 = 80$  mbar and the lower spectrum, averaged for a period of 1.4 ms, depicts post-shock conditions after arrival of the reflected shock wave at  $T_5 = 1506$  K and  $p_5 = 2.4$  bar.



Figure 2. Pressure traces for representive experiments using driver length variation (black: 0 cm; blue: -60 cm, red: -80 cm at  $T_5 = 1490$  K,  $p_5 = 1.5$  bar).

Besides the parent peak of cyclohexene at m/z = 82, 45 eV electron impact ionization leads to fragmentation with the dominant signal at m/z = 67 (C<sub>5</sub>H<sub>7</sub>) and smaller peaks at m/z = 54 an 28. The peaks at m/z = 40 and 128–136, respectively, are related to the internal standards Ar and the Xe isotopes, respectively. Parent product peaks belong to butadiene at m/z = 54 and to ethylene at m/z = 28. The change in ratio of the C<sub>2</sub>H<sub>4</sub> and C<sub>4</sub>H<sub>6</sub> peak areas relative to the C<sub>6</sub>H<sub>10</sub> peak area between pre- and post-shock reflects decomposition of C<sub>6</sub>H<sub>10</sub> and formation of C<sub>2</sub>H<sub>4</sub> and C<sub>4</sub>H<sub>6</sub>.

To follow the time profile of cyclohexene in the HRR-TOF-MS experiments, we used the major cyclohexene fragment peak at m/z = 67. To extract the rate coefficient k for R1 from the cyclohexene time profile, we used a function representing a single-exponential decay with an offset as the fit function:

$$\frac{I_{CSH7}}{I_{Ar}} = A + B \exp(-k t).$$
(1)



Figure 3. Mass spectra for pre-shock conditions averaged for t = 0.6 ms at  $T_1 = 295$  K and  $p_1 = 80$  mbar (top) and post-shock conditions averaged for a period of 1.4 ms at  $T_5 = 1506$  K,  $p_5 = 2.4$  bar (bottom) conditions. The repetition rate of ionization was 100 kHz and the energy of ionizing electrons was 45 eV. The pre-shock spectrum was inverted and multiplied by 5 for better illustration.

Figure 4 shows an experimental cyclohexene concentration-time profile along with a fit according to eq. 1. The use of an offset was necessary because the signal did not completely decay back to the baseline even after the decomposition according to literature rate coefficients was essentially complete. The reason for this behavior is unclear at the moment and requires further investigations.



Figure 4. Intensity-time profile of  $C_6H_{10}$ , probed by following the fragment ion signal at m/z = 67, and a fit using eq. R2 ( $T_5 = 1500$  K and  $p_5 = 2.4$  bar, 0.25%  $C_6H_{10}$ , 0.25% Ar, 0.25% Xe in Ne).

The low mole fraction ( $\leq 0.25\%$ ) of C<sub>6</sub>H<sub>10</sub> in these experiments allowed the direct determination of the rate coefficient from the fit according to eq. 1, because the temperature change due to heat of reaction was minor ( $\leq 10$  K). In addition, we performed experiments using higher mole fractions of C<sub>6</sub>H<sub>10</sub> (1-2%). Here the

heat of reaction substantially altered the temperature during decomposition of  $C_6H_{10}$ .



Figure 5. Concentration-time profiles for the post-shock region for experiment at  $T_5 = 1407$  K and  $p_5 = 1.56$  bar. Black squares are  $C_2H_4$ , red squares are  $C_6H_{10}$ , solid lines are the corresponding simulations. Mixture: 1%  $C_6H_{10}$  with 1% Ar in Ne.

To account for non-isothermal conditions, we simulated these experiments at high concentrations using the reflected shock model from CHEMKIN. As initial estimate we used the Arrhenius equation determined in the experiments with concentrations of 0.1-0.25%. With this factor the rate coefficient was calculated for a temperature which was most sensitive for the concentration decay of C<sub>6</sub>H<sub>10</sub> in the experiment. Good agreement of our GC data and TOF data with low and high concentration was found. All these data agree very well with literature measurement using different detection techniques.

#### Conclusions

The decomposition of cyclohexene at high temperature was studied with a single-pulse shock tube coupled with HRR-TOF-MS and GC. From HRR-TOF-MS measurements using dilute  $C_6H_{10}$  mixtures, rate coefficients were directly determined by fitting a first-order exponential decay to the experimental  $C_6H_{10}$  time profile. Simulations of the time profiles in experiments using larger  $C_6H_{10}$  mole fractions (1-2%) required taking into account non-isothermal effects during cyclohexene decomposition. Additionally, GC measurements provided further information about the decomposition. All our measurements show a good agreement to each other and to literature values based on different detection techniques like single-pulse<sup>11</sup>, TOF-MS<sup>12</sup>, laser-Schlieren<sup>5</sup> and infrared  $C_2H_4$  absorption measurements<sup>6</sup>.

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# FIRST-PRINCIPLES BASED GROUP ADDITIVITY VALUES FOR THERMOCHEMICAL PROPERTIES OF SUBSTITUTED AROMATIC COMPOUNDS

<u>A. Ince</u>, H.-H. Carstensen, M.-F. Reyniers and G.B. Marin Laboratorium voor Chemische Technologie - Universiteit Gent, *Technologiepark 914, B-9052 Zwijnaarde, Gent, Belgium.* 

#### Abstract

A set of 7 Benson group additive values (GAV) together with 15 correction terms for non-nearest neighbor interactions (NNI) is developed to calculate the gas phase standard enthalpies of formation, entropies and heat capacities of substituted monocyclic aromatic molecules containing methyl, ethyl, vinyl, formyl, hydroxyl and methoxy substituents. These GAVs are obtained through least squares regression of a database of thermodynamic properties of 143 molecules, calculated at the post-Hartree–Fock G4 composite method. Out of the 15 NNIs, which account for several well-known substituent effects in aromatic molecules, 13 have been determined for the first time. All but two group additively calculated standard enthalpies of formation agree within 4 kJ mol<sup>-1</sup>, and the entropies and heat capacities generally deviate by less than 4 J mol<sup>-1</sup> K<sup>-1</sup> from the ab initio results. Natural bond orbital (NBO) analysis is utilized to identify the underlying causes of the observed NNIs.

## Keywords

Thermochemistry, group additivity, monocyclic aromatic hydrocarbons.

# Introduction

Thermodynamic properties of molecules such as their standard enthalpy of formation  $(\Delta_f H^{\circ})$ , entropy  $(S^{\circ})$  and heat capacity  $(\mathcal{C}_{p})$  play a pivotal role in the construction of fundamental kinetic models. Current interests in the thermochemical conversion of biomass to liquid fuels or commodity chemicals leads to the need for kinetic models that describe the thermochemical conversion of its components cellulose, hemicellulose and lignin. Fast pyrolysis of lignin yields substituted monocyclic aromatic compounds with a limited number of substituent groups (Evans and Milne, 1987). In particular in the context of automated mechanism generation, the lack of a comprehensive experimental thermochemical data base and the high computational costs of accurate firstprinciple calculations for large aromatic molecules render alternative approaches to quickly calculate thermochemical properties worthy of consideration.

А popular approach to describe thermodynamic properties of gas phase species is the Benson's group additivity method (Benson, 1976). This method considers a molecule as an entity consisting of smaller units called groups, and uses an additive scheme to obtain thermochemical data based on contributions from these groups, which are known as "group additive values (GAVs)". Benson defines a group as "a polyvalent atom in a molecule together with all its ligands" (Benson, 1976). Although GAVs account for the major part of a thermodynamic property, additional contributions from interactions that extend beyond the range of a group have to be included as well. These so-called non-nearest neighbor interactions are incorporated as additive correction terms (NNIs). The thermodynamic property "y" thus is calculated as shown in Eq. (1).

$$y = \sum_{i=1}^{i} n_i * GAV_i + \sum_{i=1}^{j} n_i * NNI_j$$
(1)

In Eq. (1), the GAV<sub>i</sub> refer to different groups which occur  $n_i$  times in the molecule and NNI<sub>j</sub> is the j<sup>th</sup> correction term which occurs  $n_j$  times in the molecule.

The purpose of the present study is to extend the GAV and NNI database to substituted monocyclic aromatic hydrocarbons (MAHs). Since this extension is motivated by the interest in modeling pyrolysis products of lignin, the following substituent groups are considered: hydroxy (-OH), methoxy (-OCH<sub>3</sub>), formyl (-C=O), vinyl (-C=CH<sub>2</sub>) and methyl (-CH<sub>3</sub>) and ethyl (-CH<sub>2</sub>CH<sub>3</sub>). The following approach is adapted: (i) A database of accurate gas phase standard enthalpies of formation  $(\Delta_f H^\circ)$ , entropies  $(S^\circ)$  and heat capacities  $(C_p(T))$  for a set of 133 molecules is constructed using high level electronic structure calculations. (ii) The necessary GAVs are identified and preliminary values are assigned based on the data for mono-substituted benzenes. (iii) Deficiencies in the group additively calculated data are used to identify those non-nearestneighbor interactions (NNIs) that contribute significantly to the thermodynamic properties. (iv) Natural Bond Orbital (NBO) analyses is carried out to support the NNI selections. (v) All unknown GAV and NNI parameters are finally simultaneously optimized to best reproduce the thermodynamic data of the entire reference data set.

#### Methodology

The Gaussian 09 software package (Gaussian, 09) has been used to perform all electronic structure calculations. Thermodynamic properties are calculated at CBS-QB3 (Montgomery et al., 1999) and G4 (Curtiss et al., 2007) levels of theory. In order to take thermochemical effects due to rotation of single bonds into consideration, the one dimensional hindered rotor (1D-HR) approach of Van Speybroeck and coworkers (Van Steenkiste et al., 2003) is applied.

The atomization energy method (Curtiss et al., 1997) is utilized to obtain standard enthalpies of formation ( $\Delta_f H^\circ$ ). Two different types of corrections have been applied to these energies. First, spin-orbit (SO) corrections of 0.35 kJ mol<sup>-1</sup> per carbon atom and 0.93 kJ mol<sup>-1</sup> per oxygen atom (Curtiss et al., 1997) have been applied to the results from the CBS-QB3 calculations only since SO corrections are part of the G4 methodology (Curtiss et al., 2007). Second, "Bond Additive Corrections" (BACs) (Petersson et al., 1999) are applied to eliminate the remaining systematic errors of ab-initio calculations as given in Eq. (2).

$$\Delta_{f}H^{\circ}(BAC) = \Delta_{f}H^{\circ}(ab - initio) + \sum_{ij}N_{ij}BAC_{ij}$$
 (2)

In Eq. (2), *i* and *j* run over the two different atom types and  $N_{ij}$  is the number of bonds between atoms of type *i* and *j*. As both CBS-QB3 and G4 methods suffer from different systematic bond-related errors, BAC values were developed separately for both methods from a training set of 77 molecules for which reliable experimental data is available.

The symmetry-independent "intrinsic" entropies  $S_{int}$  are used in forming the thermochemical database.  $S_{int}$  is calculated as given in Eq. (3).

$$S_{int}^{\circ} = S^{\circ} + R \ln\left(\frac{\sigma}{n_{opt}}\right)$$
 (3)

where  $\sigma$  is the global symmetry number and  $n_{opt}$  is the number of optical isomers. The global symmetry number  $\sigma$  is the product of external symmetry number  $\sigma_{ext}$  and the internal symmetry numbers  $\sigma_{int}$ , as given in Eq. (4).

$$\sigma = \sigma_{ext} \prod_k \sigma_{int,k} \tag{4}$$

### **Results and Discussion**

#### Formation of Thermochemical Databases

CBS-QB3/BAC and G4/BAC calculations have been performed to construct databases of accurate gas phase ( $\Delta_f H^\circ$ ), entropies ( $S^\circ$ ) and heat capacities ( $C_p(T)$ , with T = 300 K, 400 K, 500 K, 600 K, 800 K, 1000 K and 1500 K) for 133 monocyclic aromatic hydrocarbons. The sets include benzene, six single substituted benzenes, all possible 63 double substituted benzenes and 63 triple substituted benzenes. A comparison of the BAC-corrected standard enthalpies of formation obtained at both levels of theory reveals that both datasets agree well with each other. The Mean Average Deviation (MAD) between CBS-QB3 and G4 datasets is 1.19 kJ mol<sup>-1</sup> and only for a few molecules the  $\Delta_f H^\circ$  values deviate by more than 4 kJ mol<sup>-1</sup>. The MAD for intrinsic entropies ( $S_{int}^\circ$ ) is 0.63 J mol<sup>-1</sup> K<sup>-1</sup> and that for the heat capacities ( $C_p$ ) at 300 K is 0.4 J mol<sup>-1</sup> K<sup>-1</sup>.

Based on the good agreement, either database is suitable to determine the group additivity parameters (GAV, NNI) for the MAHs of interest. However, CBS-QB3 calculated bond dissociation energies for the C-H bond in benzene (483.0 kJ mol<sup>-1</sup>), the C-O bond in phenol (480.7 kJ mol<sup>-1</sup>) and the aryl-CHO bond in benzaldehyde (428.2 kJ mol<sup>-1</sup>) deviate by more than 10 kJ mol<sup>-1</sup> from well-established experimental values  $(472.2 \pm 2.2 \text{ kJ mol}^{-1}, {}^{36} 465.7 \pm 4.2 \text{ kJ mol}^{-1} {}^{36} \text{ and} 415.5 \pm 3.8 \text{ kJ mol}^{-1}, {}^{37} \text{ respectively})$ . This casts doubts on the ability of the CBS-QB3 method to accurately describe aromatic molecules. With respect to the bond dissociation energies mentioned above, G4 yields those values to be 471.1 kJ mol<sup>-1</sup>, 465.1 kJ mol<sup>-1</sup> and 414.2 kJ mol<sup>-1</sup>, respectively, in excellent agreement with the experimental data. Since the G4 method is more reliable for radicals from MAHs than CBS-OB3. the G4 database will be utilized as reference thermochemical database in this study.

#### Assignment of initial GAVs

In total 14 GAVs are required for the GA calculation of the thermodynamic properties of the 133 MAHs of the reference dataset. Among these, there are 3 GAVs, namely  $C(O)(H)_3$ ,  $C(C)(H)_3$  and  $C_d(H)_2$ , that describe non-aromatic moieties. The values for these GAVs are taken from earlier studies (Sabbe et al. (2005), Sabbe et al. (2008) and Paraskevas et al. (2013)) to ensure internal consistency with previous work. In order to eliminate linear dependencies, the values for 4 GAVs;  $O-(C_b)-(H)$ ,  $CO-(C_b)-(H)$ ,  $C_d-(C_b)-(H)$  and  $C-(C_b)-(H)_3$  GAVs are set equal to the structurally similar GAVs  $O-(C_d)-(H)$ ,  $CO-(C_d)-(H)$ ,  $C_d-(C_d)-(H)$  and  $C-(C_d)-(H)_3$ .

The preliminary GAVs have been used to calculate the  $\Delta_f H^\circ$  and  $S^\circ$  values of all 63 double substituted benzenes in the reference database. Comparison with the reference data revealed that some  $\Delta_f H^\circ$  values deviated by more than 20 kJ mol<sup>-1</sup>. In one case, a large entropy difference of 23.1 J mol<sup>-1</sup> K<sup>-1</sup> was observed. This clearly shows that non-nearest neighbor interactions (NNI) need to be accounted for to obtain reliable data from GA calculations.

# Identification of NNIs

The NNIs that are identified from the deviations between ab initio and GA calculations are given in Table 1 along with the possible origin of these interactions. The Natural Bond Orbital (NBO) method

of Weinhold and coworkers has been employed to interpret the underlying physical origin of these NNIs. (NBO, 6.0).

Table 1. Non-nearest neighbor interactions (NNIs) identified from the differences between GA predictions using preliminary GAVs and the reference data.

NNI	Interacting substituents	Contributions to NNI
NNI1	o-OH+ CHO	HB <sup>[a]</sup> , Mesomeric, Inductive
NNI2	o-CHO+ CHO	HB, Mesomeric, Inductive
NNI3	o-MeO+MeO	Anomeric, Mesomeric, Inductive
NNI4	o-CH=CH <sub>2</sub> + CHO	Steric, Inductive
NNI5	o-CH=CH <sub>2</sub> + CH=CH <sub>2</sub>	Steric, Inductive
NNI6	p-OH/MeO+ OH/MeO	Mesomeric, Inductive
NNI7	p-CHO+ CHO	Mesomeric, Inductive
NNI8	o-Me/Et+ CHO	Steric, Mesomeric, Inductive
NNI9	o-CH=CH <sub>2</sub> + Me/Et	Steric
NNI10	m-CHO+ CHO	Inductive
NNI11	p-CHO+ OH/MeO	Mesomeric, Inductive
NNI12	o-MeO+ CHO	HB, Mesomeric, Inductive
NNI13	o-Me/Et+ Me/Et	Steric
NNI14	o-OH+ OH/MeO	HB, Mesomeric, Inductive
NNI15	o-CH=CH2+ OH/MeO	Steric, Inductive
<sup>[a]</sup> HB: H	lydrogen Bond	

11 out of 15 NNIs are needed to correct for substituent interactions in ortho position. This indicates the important role of steric or short distance interactions on the thermodynamic properties. Three NNIs describe interactions of substituents in para position and one in meta position.

In the following, the physical phenomena that cause the three strongest non-nearest neighbor interactions is discussed. In NNI1, NBO analysis shows the stabilization energy due to the hydrogen bonding to be -23.5 kJ mol<sup>-1</sup>. The +M character of CHO and the -M effect of the OH lead to additional stabilization. The presence of these two stabilizing interactions explain the high deviation of -28.7 kJ mol<sup>-1</sup> between ab-initio and GA calculation results. In NNI2, the strong electron withdrawing -M and -I effect of formyl groups are the reason why the presence of two formyl groups in ortho position destabilize the molecule by 20.4 kJ mol<sup>-1</sup>. A weak hydrogen bond (calculated stabilization of -6.4 kJ mol<sup>-1</sup>) only partially compensates the destabilizing resonance interaction. NNI3 describes the repulsion between the lone pairs on the oxygen atoms of two OCH<sub>3</sub> groups in o- position relative to each other, e.g. anomeric effect. Further destabilization results from the combination of +M and -I effects of both groups, hence NNI3 significantly increases the enthalpy of formation.

#### Simultaneous determination of GAVs and NNIs

In order to improve the predictions, GAVs are in the next step optimized simultaneously with the identified NNI parameters via least squares fitting using the information of the entire training set. The MAD for the  $\Delta_f H^\circ$  of the reference data set of 133 molecules is 0.95 kJ mol<sup>-1</sup>, and those for the *S*° and *C*<sub>p</sub> predictions are 1.60 J mol^{-1}  $K^{\text{-1}}$  and <1.56 J mol^{-1}  $K^{\text{-1}},$  respectively.

# Validation of the GAVs and NNIs

The transferability of the simultaneously optimized GAVs and NNIs is tested with a test set consisting of 9 triple substituted, 13 quadruplesubstituted and 3 quintuple substituted MAHs. Due to the higher computational cost for the G4 method, ab initio data for 12 quadruple-substituted and three quintuple substituted MAHs could only be obtained with the CBS-QB3/BAC method whereas the remaining 10 molecules were calculated at the G4/BAC level. The statistics of this test underlines the good performance of the new GAV/NNI set. The MAD values of 1.8 kJ mol<sup>-1</sup> ( $\Delta_f H^\circ$ ) and 3.0 J mol<sup>-1</sup> K<sup>-1</sup> and 2.4 J mol<sup>-1</sup> K<sup>-1</sup> for  $S^{\circ}$  and  $C_p(300 \text{ K})$  respectively, show that the group values are transferable and that the calculated thermodynamic properties are highly accurate even for highly substituted benzenes with strongly interacting substituents.

# Determination of the final set of GAVs and NNIs

The aforementioned 10 molecules in the test set for which ab initio data are available at the G4 level were added to the training set of 133 molecules and the final GAV and NNI parameters are obtained through a linear regression analysis on the data set of 143 molecules.

The MAD between the GA and ab initio calculated data of the  $\Delta_f H^\circ$  for the 143 molecules is 0.93 kJ mol<sup>-1</sup>, and those for the  $S^\circ$  and  $C_p$  data are 1.66 J mol<sup>-1</sup> K<sup>-1</sup> and < 1.56 J mol<sup>-1</sup> K<sup>-1</sup>, respectively.

The distribution of the difference between the reference and the GA calculated data for  $\Delta_f H^\circ$  and  $S^\circ$  is shown in Figures 1 and 2, respectively. Almost all of the 143 enthalpies of formation obtained by GA are within 4 kJ mol<sup>-1</sup>. Similarly, the entropies differ generally by less than 4 J mol<sup>-1</sup> K<sup>-1</sup>.



Figure 1. Distribution of the differences between final GA and G4  $\Delta_f H^\circ$  values for the molecules in the reference set,  $\Delta \Delta_f H^\circ((NNI+GAV)-G4)$ .





#### Conclusions

A set of 7 GAV and 15 NNI has been derived to obtain the thermodynamic properties of monocyclic aromatic hydrocarbons with six substituents: hydroxy (-OH), methoxy (OCH<sub>3</sub>), formyl (-C=O), vinyl (-CH=CH<sub>2</sub>) and the alkyl groups methyl (-CH<sub>3</sub>) and ethyl (-CH<sub>2</sub>CH<sub>3</sub>). The GAV and NNI parameters were determined from a set of 143 molecules (reference data), whose thermodynamic values were calculated with bond additivity corrected (BAC) G4 theory. The BAC values were obtained as part of this study from a set of 77 molecules, for which accurate experimental data exist. Computations with the CBS-QB3 method yielded similar results, which indicates that the CBS-QB3 method is reliable for closed-shell aromatic molecules and observed problems with bond dissociation energies are caused by problems to describe the phenyl radical accurately.

NNIs were found to be crucial to achieve accurate group additivity calculations. NBO calculations were employed to ensure that the defined NNIs are meaningful and to provide insight into the type of interactions that cause either stabilization or destabilization. Values obtained with the optimized GAV and NNI parameters agree very well with the reference data set. The mean absolute deviations (MAD) are 0.93 kJ mol<sup>-1</sup> for  $\Delta_f H^{\circ}$ , 1.66 J mol<sup>-1</sup> K<sup>-1</sup> for  $S^{\circ}$  and less than 1.56 mol<sup>-1</sup> K<sup>-1</sup> for  $C_p$  values at all studied temperatures. All group additivity based enthalpies are within 5 kJ mol-1 for the ab initio values and only for two molecules, the deviation exceeds 4 kJ mol<sup>-1</sup>. Similarly, the entropies are for almost all molecules reproduced to within 4 J mol<sup>-1</sup> K<sup>-1</sup>, which demonstrated the high accuracy obtained with the GAV/NNI set calculated in this study. Further validation using nine triple-substituted, thirteen quadruple-substituted and one quintuple-substituted benzene underscored the predictive capability. Combined with previously published GAV for hydrocarbon and oxygenated hydrocarbon species, an internally consistent set of group additivity parameters is now available for closed-shell monocyclic aromatic

molecules. This work is currently extended towards substituted monocyclic aromatic radicals.

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### **PHOTODISSOCIATION OF METHANOL AT 193.3 NM**

Chao Yan<sup>\*</sup>and Lev N. Krasnoperov New Jersey Institute of Technology Newark, NJ 07102

#### Keywords

Kinetics, Quantum yield, Absorption cross section, Methoxy radical.

Methanol,  $CH_3OH$ , is characterized as a photolytic source of methoxy radical ( $CH_3O$ ) for kinetic studies. The major channel of photodissociation of methanol at 193.3 nm is channel 1a, forming methoxy and hydrogen atom.<sup>1</sup> Presumably a minor channel producing  $CH_3$  and OH (1b) is not well characterized. In this work, the quantum yield of channel 1b was measured:

CH <sub>3</sub> OH	+	hv (193.3 nm)	
Н	+	CH <sub>3</sub> O	
CH <sub>3</sub> O	+	CH <sub>3</sub> O	

The approach is based on the ArF excimer laser photolysis coupled to UV-vis transient absorption spectroscopy and a high-pressure flow system.

In photolysis of methanol methyl radicals could be produced both in direct photolysis 1b and in the fast secondary reaction 2 of hydrogen atoms with methoxy radicals.

Transient absorption profiles of CH<sub>3</sub>, OH and CH<sub>3</sub>O were recorded in the photolysis of CH<sub>3</sub>OH/H<sub>2</sub>O/He gas mixtures at 193.3 nm. Methyl radicals were monitored via absorption at 216.4 nm; hydroxyl radicals were monitored via absorption at ca. 308 nm and methoxy radicals via absorption at ca. 298.4 nm.

$\rightarrow$	CH <sub>3</sub> O	+	Η	(1a)
$\rightarrow$	CH <sub>3</sub>	+	OH	(1b)
$\rightarrow$	CH <sub>3</sub>	+	Н	(2)
$\rightarrow$	products			(3)



Figure 1

The results at ambient temperature and pressure (296 K, 1.01 bar, He) are shown in Figure 1 (stars), together with the results of the previous experimental study (upper limit)<sup>1</sup> (squares). The quantum yield of channel 1b is  $\phi_{1b} = (2.0 \pm 0.5) \times 10^{-2}$ . Preliminary results are also obtained for the sum of the rate constant of reaction 2 and 3,  $k_2 + 2k_3 = (2.3 \pm 1.0) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Extension of the study to higher temperatures (up to 834 K) as well as pressures (up to 100 bar) is in progress.

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### STUDY OF OH RADICAL KINETICS RELEVANT FOR DIMETHYLETHER COMBUSTION USING THE FAGE TECHNIQUE

#### Lavinia Onel<sup>\*</sup>, Mark Blitz, David Potter and Paul Seakins University of Leeds Leeds, LS2 9JT

Keywords dimethylether, combustion, OH kinetics, FAGE technique

Dimethylether (CH<sub>3</sub>OCH<sub>3</sub>, DME) has considerable potential as a fuel, but there are significant uncertainties in the mechanism of its important low temperature combustion. Limitations in previous studies include a lack of real-time observation of radicals. A key intermediate species is OH radical. We use a novel high temperature (up to ~800 K) and high pressure (to ~ 5 atm) instrument to measure OH kinetics. Reactions are initialized by laser flash photolysis of suitable precursors (e.g.  $(COCl)_2 + h\nu (\lambda = 248 \text{ nm}) / DME$ ). The reaction mixture is sampled through a pinhole from a high pressure (2 atm) heated flow reactor to a low pressure cell (FAGE cell at 1 Torr) for detection of OH by laser induced fluorescence in the gas expansion producing a supersonic jet.<sup>1</sup>

The proposed mechanism for the chain branching process leading to auto-ignition in the low temperature combustion of DME is illustrated schematically ( $R = CH_3OCH_2$ ,  $Q = CH_2OCH_2$ ):  $R + O_2 \Leftrightarrow RO_2 \Leftrightarrow QOOH \xrightarrow{O2} O_2QOOH \rightarrow 2OH + products$ . The limits for branching in DME oxidation are determined by the competition between QOOH reacting with  $O_2$  leading to the chain branching step, which produces two OH, and decomposing in a chain propagation step, QOOH  $\rightarrow OH + CH_2O$ . This competition is controlled by the concentration of  $O_2$ . Comparison of experimental kinetic traces at 560 K (Figure 1a) with the OH time evolution obtained by numerical simulations using a chemistry scheme consisting of literature reactions and rate coefficients<sup>2, 3</sup> (Figure 1b) requires small adjustments in the description of the CH<sub>3</sub>OCH<sub>2</sub> + O<sub>2</sub>/DME system to reproduce the OH measurements. These are the first direct measurements of QOOH chemistry in DME low temperature combustion.



Figure 1. Rise of the maximum level of the measured OH signal (a) and the modeled concentration of OH (b) by increasing  $[O_2]/cm^{-3}$  from  $10^{17}$  to  $3 \times 10^{18}$  in the CH<sub>3</sub>OCH<sub>2</sub> + O<sub>2</sub>/DME system at 560 K and 2 atm. The rise is due to the increasing contribution of the QOOH + O<sub>2</sub> reaction to the generation of OH with increasing  $[O_2]$ .

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### THERMAL DECOMPOSITION OF GRAPHENE OXYRADICALS UNDER THE INFLUENCE OF AN EMBEDDED FIVE-MEMBERED RING

Hongmiao Wang,<sup>a, b</sup> Hong-Bo Zhang,<sup>a, b</sup> Michael J. Pilling,<sup>c</sup> Xiaoqing You<sup>a, b\*</sup> <sup>a</sup> Center for Combustion Energy, Tsinghua University, Beijing, 100084, China <sup>b</sup> Key Laboratory for Thermal Science and Power Engineering of Ministry of Education, Tsinghua University, Beijing 100084, China <sup>c</sup> School of Chemistry, University of Leeds, Leeds LS2 9JT, UK

#### Abstract

In this study, we examine the influence of an embedded five-membered ring on the thermal decomposition of graphene oxyradicals. Their decomposition potential energy surfaces were explored at the B3LYP/6-311g(d,p) level. The temperature and pressure dependence of the rate coefficients was computed by master equation modeling. The results suggest that the embedded five-membered ring leads to a generally slower decomposition rate for CO elimination than that of graphene oxyradicals with only six membered rings, and the impact of the embedded five-membered ring are two layers away from the edge.

#### Keywords

Soot Surface Oxidation, Five-Membered Ring, Thermal Decomposition

#### Introduction

Surface reactions, controlling soot mass growth rate in flames, have received continuing attention in recent years. Considering the similarity between soot particle surfaces and graphene edges, chemical similarity is usually invoked. Consequently, the reactions of polycyclic aromatic hydrocarbons (PAHs) have been used to model soot surface reactions. Surface reactions consist of both growth and oxidation reactions. It has been recognized that the growth of carbon mass follows the hydrogenabstraction-C<sub>2</sub>H<sub>2</sub>-addition (HACA) mechanism (Frenklach and Wang, 1991) and the five-membered ring is possible to be fully enclosed or embedded into the growing layer, leading to a curved structure (Whitesides and Frenklach, 2010). Previous studies on the oxidation of both small aromatics and large PAHs suggested that the most dominant pathway for PAH and graphene oxidation at high temperatures is the formation of oxyradicals and their subsequent decomposition which eliminates CO (Kunioshi et al., 2002). Oxyradicals are thus the major intermediates and their decomposition is one of the key steps. You et al. (2011) and Edward et al. (2013) examined the thermal decomposition of oxyradicals occurring on a zigzag and an armchair edge, respectively. Their results show that there are mainly two pathways for the decomposition. One is called electrocyclic mechanism, the other is called ring-opening mechanism. Considering that an embedded five-membered ring plays an important role in the soot surface growth, we ponder its influence on the oxidation reactions especially the decomposition of

oxyradicals. A very recent study (Singh et al. 2015) investigated the oxidation by molecular oxygen of a graphene edge with a five-membered ring at the corner of the reacting layer and concluded that its dominant pathway is eliminating CO<sub>2</sub> rather than CO and with a rate that is relatively low compared to the oxidation of six-membered rings. In this study, we intend to investigate systematically the decomposition kinetics of PAH oxyradicals containing an embedded fivemembered ring, and study the influence of an embedded five-membered ring on the decomposition of oxyradicals. For this purpose, we selected seven typical PAH oxyradicals containing an embedded fivemembered ring, representing different surface active sites of a soot particle, and then explored the potential energy surfaces at the same level of theory as our previous studies (You et al., 2011, Edwards et al., 2013), and computed the rate coefficients over the ranges of 1500-2500 K and 0.1-10 atm by solving the master equations.

#### **Computational Methodology**

The potential energy surfaces of the unimolecular decomposition of all oxyradicals were computed using the density functional theory. Geometry optimization and vibrational frequency calculations were performed using the B3LYP hybrid functional with the 6-311G (d,p) basis set. Hindered rotors corrections were performed at the same level of theory but with a smaller basis set, 6-31G (d). Zeropoint energies and vibrational frequencies were scaled by a factor of 0.967 (Johnson, 2005). All quantum-chemical calculations were carried out using the

<sup>•</sup> Corresponding author: *xiaoqing.you@tsinghua.edu.cn* 430

Gaussian 09 program package (Frisch et al., 2010). The reaction systems for each oxyradical were calculated for temperatures ranging from 1500 to 2500 K and pressures from 0.1-10 atm. We used two different master equation programs, Multiwell suite of package (Barker, 2001) and MESMER (Glowacki et al., 2012). The thermal decomposition rate coefficients were derived from the exponential decay profile of the reactant molecule after a period of initial relaxation. Argon was chosen as the bath gas collider. The Lennard-Jones parameters  $\sigma$  and  $\varepsilon/k_{R}$  of argon were 3.47 and 114 respectively, while for other species they were estimated from an empirical correlation proposed by Wang and Frenklach (1994). The exact count, with an energy grain size of 10 cm<sup>-1</sup> for the first segment of the double array, and a maximum energy of 300000 cm<sup>-1</sup>, was employed in Multiwell [21-23] calculations. While a grain size of 100 cm<sup>-1</sup> was set for MESMER. The exponential-down model with a constant  $<\Delta E_{down} > = 260 \text{ cm}^{-1}$  was used.

#### **Results and Discussion**

# Oxyradicals containing an embedded five-membered ring

A total of seven oxyradicals, denoted hereafter as oxyradical a-g as shown in Figure 1(h), were selected to represent oxyradicals containing an embedded five-membered ring. Substitution of H by O at different positions of benzo[ghi]fluoranthene leads to oxyradicals a-e, which represent an oxidized graphene edge with an embedded five-membered ring in the top carbon layer. Comparison between oxyradicals a-e can reveal how the effect of the fivemembered ring changes with different O atom chemisorption sites along the top layer. Oxyradical f is generated from oxidation of corannulene, which represents a graphene edge with a five-membered ring completely embedded in the interior carbon layer. Extension of one additional carbon layer of oxyradical f leads to oxyradical g, which represents a graphene edge with a five-membered ring embedded two layers away from the edge. Comparison of the two can reveal if the embedded five-membered ring still has an impact when it is farther away from the edge.

#### Minimum energy pathways

We explored the potential energy surfaces at the B3LYP/6-311G(d,p) level of the seven oxyradicals. Our results indicate that, due to the influence of the embedded five-membered ring, the decomposition pathways of all the oxyradicals show different characteristics from those six-membered rings oxyradicals studied before (You et al., 2011, Edwards et al., 2013), however, the influence diminishes as the location of O atom is farther away from the embedded five-membered ring. Figure 1(a) shows the multi-path and multi-product potential energy surface (PES) for the decomposition of oxyradical a, in which the O atom is bonded to a neighbor C atom of the embedded fivemembered ring. It can be seen there are four main pathways, two of which are initiated by ring opening (1-6, 1-5), leading to the ring-opening intermediates 5 or 6. Intermediate 6 can either isomerize to intermediate 7 which subsequently eliminates CO, or decompose to produce  $C_2H_2$  or H, while intermediate 5 can eventually lead to the elimination of CO. Transition states TS1-7 and TS1-3 have been found, forming another two distinct pathways terminated with the elimination of CO. Seemingly CO elimination would still dominate because of the much lower energy barrier, which although is enhanced compared to the six-membered rings oxyradicals. However, the branching ratios of CO, C<sub>2</sub>H<sub>2</sub> and H elimination is likely to be temperature dependent since the influence of entropy cannot be ignored, especially at high temperatures relevant to combustion (1500-2500 K).

Figure 1(b) shows the PES for the decomposition of oxyradical b which contains two free edges. It decomposes similarly as those six-membered rings oxyradicals, which is not unexpected as O atom is located farther away from the five-membered ring. However, there are remarkable differences in detail. Figure 1(c-g) show the PESs of the decomposition for oxyradical c-g which all contain only one free edge. They proceed through similar pathways to those sixmembered rings oxyradicals eliminating CO. It is interesting that the PESs of oxyradical c-f resemble each other not only in term of pathways but also absolute energy barrier along the minimal energy paths, which is around 15 kcal/mol higher than that of the six-membered rings oxyradicals with only one free edge. To be noted, the largest radical, oxyradical t, eliminates CO with the smallest absolute energy barrier, 67.8 kcal/mol, which is very close to that of the six-membered rings oxyradicals with a comparable size, indicating that the influence of the embedded fivemembered ring on decomposition diminishes significantly as the five-membered ring is embedded in the interior layer separated from the top layer by one addition layer.

#### Master equation modelling

We computed the reaction rate coefficients of the seven systems as functions of temperature and pressure by solving the master equations. The results indicate that production of all the stable intermediates on the potential energy surfaces are negligible, except for the intermediate 5 of oxyradical f, yet which could be ignored due to a very short time scale. Inspection of the rate coefficients reveals that they are both temperature and pressure dependent. The two different programs, MESMER and Multiwell, give almost identical results. The results shown below are all from MESMER. For oxyradical a, the computed results demonstrate that the decomposition of oxyradical a is

in the fall-off region. The results indicate that the









(g)

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*Figure 1. (a)-(g): Potential energy surfaces of oxyradicals a-g calculated at B3LYP/6-311G(d,p) level (units: kcal/mol). (f): Structures of oxyradicals a-g, and pentacene oxyradicals from You et al. (2011)* 

branching ratios of  $C_2H_2$ , CO and H elimination are both temperature and pressure dependent. The  $C_2H_2$ elimination becomes more favorable than others as temperature or pressure is increased.

For oxyradical b-g, their computed rate coefficients along with that of oxyradical a at 1 atm are compared in Figure 2, in which the rate coefficient of a pentacene oxyradical is also shown. The comparison suggests that the embedded five-membered ring leads to a generally slower decomposition rate than that of the graphene oxyradicals with six-membered rings. Oxyradical g decomposes in a rate just slightly lower than pentacene II, especially at high temperatures. The comparisons among the graphene oxyradicals confirm the restraint of the embedded five-membered ring on the decomposition, whereas the influence diminishes significantly as the embedded ring is separated from the edge by an additional carbon layer.



Figure 2. Comparison of the rate coefficients of oxyradicals b-g.

#### Kinetic modelling

Considering that the reverse reactions for  $C_2H_2$ or H elimination need to be evaluated, we built a phenomenological kinetic model containing both forward and reverse reactions for oxyradical a and predicted the species profiles at different temperatures and pressures. The initial mole fractions of  $C_2H_2$ , CO and H are  $x_{CH_2} = x_{c_0} = 0.1, x_{H} = 0.01$  according to previous studies (Whitesides et al., 2010). The overall simulation time is 1 ms. Results show that at 2500 K, the mole fractions of  $C_2H_2$  and H are the largest, while at 1500 K, there is almost no accumulation of  $C_2H_2$  and H and the production of CO dominates. As for 2000 K, the species profiles of both  $C_2H_2$  and H display a trend in which the mole fractions peak at around 0.3-0.4 ms.

#### Conclusions

In this study, the influence of an embedded fivemembered ring on the thermal decomposition of graphene oxyradicals was investigated. The results suggest that the embedded five-membered ring leads to a generally slower decomposition rate for CO elimination than that of graphene oxyradicals with six-membered rings. The influence of the embedded five-membered ring diminishes significantly as the embedded fivemembered ring are two layers away from edge. In addition, the oxidation rate of the benzo[ghi]fluoranthene oxyradicals has been found to be site-dependent. When the O atom is bonded to an adjacent C atom of the fivemembered ring, acetylene elimination is more favorable than the CO elimination at high temperatures within the time scale of soot formation.

#### Acknowledgments

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### The Very Open Data Project: Characterizing Combustion Kinetic Data with ontologies and meta-data

### Edward S. Blurock<sup>\*</sup> REACTION, Lund, Sweden

Keywords: Combustion Data, ontology, XML, database, XML Schema, meta-data.

The movement of *Open Data* stems from a priority at the national, European and international levels to make scientific data, especially that that stems from public funding, freely accessible. Beyond political and financial considerations is that science thrives on interaction. With modern science, especially with the explosive use and availability of electronic media, this translates to sharing electronically data between groups. The goal of the *Very Open Data Project* is to provide a software-technical foundation for this exchange of data, more specifically to provide an open database platform for data from the raw data coming from experimental measurements or models through intermediate manipulations to finally published results. The sheer expanse of the amount data involved creates some unique software-technical challenges. One of these challenges is addressed in the part of the study presented here, namely to characterize scientific data (with the initial focus being that from the combustion kinetic community), so that efficient searches can be made. A formalization of this characterization comes in the form of schemas of descriptions of tags and keywords describing data and ontologies describing the relationship between data types and the relationship between the characterizations themselves. These will be translated to meta-data tags connected to the data points within a non-relational data of data for the community.

The combustion community of researchers is fairly unique within the scientific sector in that is an extremely diverse set of researchers composed of, among others, engineers, organic chemists, physical chemists, theoretical chemists, computational modelers, physicists, mathematicians, computer scientists, modelers, experimentalists and various combinations of them. This diversity has consequences in not only terminology used within each community, but, relevant for this study, also has consequences in the data produced and managed.

A sampling of characteristics and relationships that should be characterized is that the descriptions:

- Should have the **Type** of data: the property being described (classifications/antologies already exist): kinetic rate, temperature, entropy, pressure, ...
- Should reflect the **specific property** the data point represents: property relative to a specific molecule, reaction, model, ...
- Should reflect the **history** (time) and **origin** (research group, experiment, theoretical) of the data point
- Should simulate a "**social network**" of sharing information between groups: private data, group data, public data, proprietory data, ....
- Should reflect **interdependency** of data: data points are derived from others, they are used in other complex models
- Should reflect **quality of data**: temporary data (trying it out), optimized, modified, standard accepted data, use in a single/multiple/general models, ...

The aim of this project is to set up a *service for the management of a social network of decentralized data* for the researchers within the combustion community. The purpose of this study is to take into account the needs of data exchange within this diverse community, established through an extensive survey, and encapsulate it into a service for the community. The development and implementation of the service will be in intimate interaction within the combustion community, enhanced by activities of the European Community SMARTCATS COST Action CM1404.

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### A Detailed Cyclic Ether Oxidation Mechanism for Oxiranyl and 2-Oxetanyl Radicals: A Theoretical Study

Heng Wang, Joseph W. Bozzelli<sup>\*</sup> Department of Chemistry, New Jersey Institute of Technology Newark, NJ 07102

#### Abstract

The cyclic ethers form radicals in combustion and atmospheric oxidation, which can undergo dissociation or react with  ${}^{3}O_{2}$  to form peroxy radicals, that further react to form reactive oxygenated intermediates. Composite ab initio and Density Functional theory calculation methods are used to calculate thermochemistry of oxirane, and oxetane, and their corresponding radicals. Elementary reaction pathways for unimolecular decomposition and for oxidation of the cyclic ether radicals by addition reaction of  ${}^{3}O_{2}$  are analyzed. Unimolecular decomposition kinetics of the 2-oxiranyl and 2-oxetanyl cyclic ether radicals and their reactions with  ${}^{3}O_{2}$  to form a peroxy radical and further decomposition paths of the peroxy systems are studied. Thermochemical and kinetic parameters are developed for the oxiranyl and the oxetanyl radicals and their elementary reaction paths in the unimolecular dissociations and the oxidation steps. A chemical activation kinetic analysis using QRRK for k(E) and master equation analysis for falloff is used to calculate rate constants as a function of pressure and temperature. A reaction mechanism is used to illustrate products versus time and temperature of the isolated ether systems.

Keywords Oxiranyl, 2-Oxetanyl, Oxidation, Thermochemistry, Kinetics

#### Introduction

#### Introduction

Thermochemical properties on a number of cyclic ethers compounds have been investigated in previous studies. Auzmendi-Murua reported on enthalpies of formation, entropy, and heat capacity for a set of 3 to 5 member ring cyclic ethers, hydro-peroxides, alcohols, and peroxy radicals. Bond dissociation energy information shows the C-H bond dissociation energy decrease with increasing number of carbons in the ring. The presence of the ether oxygen in the ring stabilizes the cyclic hydroperoxides, especially when the peroxy group is bonded to the ether carbon. Auzmendi-Murua noted that the further reaction of cyclic ether radicals, proceed through ring opening β-scission reactions and oxidation reaction with <sup>3</sup>O<sub>2</sub>. However, the detailed and comprehensive thermo-chemistry and kinetic study about these two systems has not been studied yet.

Joshi et al. studied oxiranyl dissociation system with using G3B3 calculation method and estimated that breaking C-O bond to open the ring need 13.5 kcal mol<sup>-1</sup> energy. Joshi reported that the oxiranyl radical primarily dissociates to ketene and H atom.

The thermochemistry of cyclic ethers of Auzmendi-Murua's are used as reference species, and comprehensive potential energy diagram of oxiranyl unimolecular dissociation system and compares our results with data of Joshi. We also show a detailed potential energy diagram of oxiranyl oxidation system, plus the2-oxetanyl unimolecular dissociation system.

#### **Computational Method**

Quantum chemical calculations have been performed within the Gaussian09 [4] suite of programs. Each unimolecular composition reaction system is divided into four classes of reactions: ring-opening β-scissions (ROBS), intramolecular hydrogen transfer (IHT) reactions, hydrogen elimination beta-scissions (HEBS) and elimination (beta scission) reactions. Enthalpies of formations of transition states (TS) are obtained from the enthalpy of formation of reactants plus enthalpy differences between reactants and TSs regarding HEBS and dissociation reactions. The enthalpy of formation of TSs are evaluated from the average of heat of formation of reactants plus energy differences between reactants and TSs and heat of formation of products plus energy differences between products and TSs regarding ROBS reactions and IHT reactions.

**2-oxiranyl radical dissociation and oxidation system** Structure parameters, vibrational frequencies, zeropoint vibration, thermal energies, and internal rotor

potentials for stable molecules, radicals, and transition states are analyzed using the composite CBS-APNO [5] calculation method.

#### 2-oxetanyl radical dissociation system

Geometries, vibrational frequencies, and thermochemical properties of transition states of each pathway are estimated with six ab initio and DFT calculation methods: (B3LYP [6], B2PLYP [7], M06 [8], M06-2X [8],  $\omega$ B97X [9],  $\omega$ B97XD [9]). These are further coupled with three different basis sets (6-31G(d,p), 6-31+G(d,p), and 6-311+G(2d,d,p)) and results compared with CBS-QB3 [10] and CBS-APNO [5] for evaluation of the methods regarding each type of reaction.

#### **Results and Discussion**

#### **Potential Energy Diagram**

Figure 1 shows the unimolecular decompose-tion pathways of 2-oxiranyl radical. Ring opening occurs by breaking the C-O bond through a16.1 kcal mol-1 energy barrier to form vinoxy radical. Vinoxy radical then undergo intramolecular hydrogen transfer reaction resulting in an acetyl radical. Alternatively, vinoxy radical undergo hydrogen elimination reaction to form ketene. The low energy acetyl radical can fragment to methyl radical and carbon monoxide or can lose a hydrogen atom to form ketene. Enthalpy values of radical and stable products are determined by work reaction analysis.



Figure 1. Potential energy diagram for dissociation of the 2-oxiranyl radical showing the heat of formation of each pathway at 298 K. Values in red are the heat of formation of transition states for each pathway. Units: kcal mol<sup>-1</sup> (CBS-APNO level of theory)

Figure 2 illustrates the oxidation reaction of 2-oxiranyl radical with molecular oxygen. Association with molecular oxygen can form a stabilized 2-oxiranyl radical peroxy radical y(cco)-qj, well 1, with well-depth 40.46 kcal mol-1. Well 1 reacts through (i) chain branching to alkoxy radical with oxygen atom; (ii) intramolecular hydrogen shift to peroxide radicals, y(ccjo)-q, y(cjco)-q; (iii) intramolecular hydrogen shift to break C-C bond and form dioxirane methyl ether radical. The lowest energy barrier pathway is TS 3 and TS4 to fragment into ethane-dial and hydroxyl radical.



Figure 2. Potential energy diagram for oxidation reaction of the 2-oxiranyl radical with molecular 302. All values are at 298 K. All red values are the heat of formation of transition states for each pathway. Units: kcal mol<sup>-1</sup> (CBS-QB3 level of theory)

Figure 3 illustrates the unimolecular dissocia-tion pathways of 2-oxetanyl radical. The low energy barrier path is ring opening to break the C-O bond with 24.46 kcal mol-1 barrier to form an aldehyde radical, well 1. Further reaction from well 1 can 1) undergo intramolecular hydrogen transfer to form CH3CH3C•=O ; 2) loss of a hydrogen to form 2-propenal; 3) fragment to ethylene plus a formyl radical, which is the lowest energy barrier path out of this well.



Figure 3. Potential energy diagram for dissociation of the 2-oxetanyl radical showing the heat of formation of each pathway. All values are at 298 K. All red values are the heat of formation of transition states for each pathway. Units: kcal mol<sup>-1</sup> (CBS-APNO level of theory)

The enthalpy of formation of each transition state is calculated with six ab initio and DFT methods coupled with the three basis sets. These data are compared with composite CBS-APNO level of theory with examples illustrated in Figure 4.



Figure 4. PE diagram of TS8 pathway in figure 1 at 298 K. Units: kcal mol<sup>-1</sup>. <sup>a</sup> Heat of formation of TS8 under different calculation methods. <sup>b</sup> Average of Enthalpy of the TS structure same calculation but different basis set. <sup>c</sup> Average of each calculation method minus CBS-APNO values. <sup>d</sup> Ref [1]. <sup>e</sup> Ref. [13].

For the Ring Opening Beta Scission reactions, B3LYP and M06 are shown to perform more accurate calculation than B2PLYP, M06-2X,  $\omega$ B97X,  $\omega$ B97XD methods. For Intramolecular Hydrogen Transfer reactions, all the ab initio and DFT methods provide acceptable calculation of the enthalpy values. For Hydrogen Elimination Beta Scission reactions, all the ab initio and DFT methods show higher barriers compared with CBS-APNO. B2PLYP provides a reasonably good value (calculation) of TS enthalpy structure enthalpy compared the DFT methods for dissociation reactions.

#### **Kinetic parameters**

Association and addition reactions have been treated as chemical activation reactions with quantum Rice-Ramsperger-Kassel analysis for k(E) and master equation for fall-off (pressure-temperature dependent stabilization of the energized adduct. Dissociation reactions are also treated with QRRK k(E)/ME analysis.



Figure 5. Rate constant as a function of temperature under 1 atm of 2-oxiranyl radical thermal decomposition system – major pathways

Figure 5 shows under 1 atm, the ketene and carbon monoxide channels are competing. Ketene has a slight dominance at high temperatures (2000K), whereas CO dominates in the low temperature area (298 K).



Figure 6. Rate constant as a function of pressure at 298 K of 2-oxiranyl radical thermal decomposition system – major pathways

Figure 6 shows that at room temperature (298K), carbon monoxide channel is domination along with all the pressure range. Under low pressure area, rate constant of CO channel remains a constant. The second important channel is ketene pathway, which has the same trend as CO channel.



Figure 7. Rate constant as a function of temperature under 1 atm of 2-oxiranyl radical oxidation system – major pathway

Figure 7 shows five major pathways in 2-oxiranyl oxidation system. Reverse reaction back to reactants and stabilization to peroxy radical are competing at high temperature. Stabilization product dominates in the low temperature area where back reaction dominates at the high temperature.



Figure 8. Rate constant as a function of pressure at 298 K of 2-oxiranyl radical oxidation system – major pathways

Figure 8 illustrates that, at room temperature, the dominate channel is stabilization for all pressures. Reverse reaction, back to reactants, and reaction to y(cjco)-q by intramolecular hydrogen transfer transition state 3 are competing with each other at about 0.01 atm. The y(cjco)-q adduct dominates is because the energy barrier for this step.



Figure 9. ChemKin modeling of 2-oxiranyl radical at 1 atm, at 400 K, 1% 2-oxiranyl radical in the presence of 1% O2 and 98% N2.

Figure 9 shows the results of a reaction mechanism model for the 2-oxiranyl radical system which combines thermal unimolecular decomposition reactions and oxygen molecular association reaction. Stabilization of 2-oxiranyl radical to peroxy radical and dissociation to carbon monoxide channels are competing with each other under 1 atm, at 400 K, react with O2 in the ratio of 1:1.



Figure 10. Rate constant as a function of temperature under 1 atm of 2-oxetanyl radical thermal decomposition system – major pathways

Figure 10 illustrates the six important pathways for decomposition of 2-oxetanyl radical. Aldehyde radical sitting in well 1 are competing with ethylene formation at 400 K. Under 1 atm, aldehyde radical has slight preponderance at room temperature, where the ethylene channel dominates at higher temperatures.



Figure 11 Rate constant as a function of pressure at 298 K of 2-oxetanyl radical thermal decomposition system – major pathways

Figure 11 illustrates near 1 atm, the aldehyde radical of well 1 is with ethylene formation at room temperature. The aldehyde radical channel dominates under higher pressure, whereas ethylene accumulates under low pressure.



Figure 12. ChemKin modeling of dissociation reaction of 2-oxetanyl radical at 1 atm, at 500 K, 5% 2-oxtanyl radical in the presence of 95% N2.

Figure 12 illustrates Chemkin modeling at 1 atm, 500 K, with 5% of 2-oxetanyl radical and 95% gas bath, ethylene is the major product. Well 1 competes with ethylene at the beginning and decreases gradually approaching near constant value for equilibrium.

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# On the reaction of isoprene hydroxyl-peroxy radicals with HO<sub>2</sub> radicals

Emmanuel Assaf<sup>\*</sup>, Coralie Schoemaecker and Christa Fittschen University of Lille 1 Villeneuve d'Ascq, France 59777

Keywords

Peroxy radicals, Isoprene, laser photolysis, cw-CRDS

Peroxy radicals (RO<sub>2</sub>) are key intermediates in the oxidations processes of Volatile Organic Compounds (VOCs). With approximately 500 Tg emitted from plants to the Earth's atmosphere each year, isoprene (2-methyl-1,3-butadiene) is the most abundant natural VOC (Guenther et la. 2006)

In low NOx environment (i.e. far from urban areas), the oxidation of isoprene in the atmosphere during daylight time is primarily initiated by the reaction with hydroxyl radical OH, rapidly followed by the addition of  $O_2$  leading to the formation of different isomers of the isoprene hydroxyl-peroxy radical (IsoO<sub>2</sub>):

Isoprene +  $OH \rightarrow Isoprene-OH$ 

Isoprene-OH + 
$$O_2 \rightarrow IsoO_2$$

The fate of  $IsoO_2$  radicals is mostly determined by reactions with NOx,  $HO_2$  or other peroxy radicals or by isomerization (Crounse et al. 2011). The reaction with  $HO_2$ :

 $IsoO_2 + HO_2 \rightarrow products$ 

is an important sink for both IsoO<sub>2</sub> and HO<sub>2</sub> species. However the rate constant of this reaction has been measured only one time,  $k(298K) = 1.7 \times 10^{-11} \text{ cm}^3$ .molecule<sup>-1</sup>.s<sup>-1</sup> (Boyd et al. 2003).

In order to get a second measurement for this important rate constant, our set-up will be used to simultaneously follow the concentrations of OH, HO<sub>2</sub> and IsoO<sub>2</sub> radicals. HO<sub>2</sub> and IsoO<sub>2</sub> radical concentrations will be measured time resolved by 2 independent continuous-wave Cavity Ring-Down Spectroscopy (cw-CRDS) paths while OH will be measured by high repetition rate Laser Induced Fluorescence (LIF), all coupled to one laser photolysis cell. The initial concentration of OH will be produced by pulsed laser photolysis of H<sub>2</sub>O<sub>2</sub> at 248nm. In absence of isoprene, the produced OH will then react with H<sub>2</sub>O<sub>2</sub> to produced HO<sub>2</sub>:

$$H_2O_2 + hv (248nm) \rightarrow 2 \text{ OH}$$

$$OH + H_2O_2 \rightarrow HO_2 + H_2O$$

Addition of isoprene and  $O_2$  will lead to the simultaneous formation of  $HO_2$  and  $IsoO_2$ , whereby the concentration of  $HO_2$  and  $IsoO_2$  will depend on the ratio of initial  $H_2O_2$  and isoprene concentrations. Results will be presented.

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### Quantum Chemical and Kinetic Study of the Oxidation Mechanisms of Naphthalene Initiated by Hydroxyl Radicals. I. The H Abstraction Pathway

Abolfazl Shiroudi<sup>*a*</sup>, Michael S. Deleuze<sup>*a*,\*</sup>

<sup>a</sup> Center of Molecular and Materials Modelling, Hasselt University, Agoralaan, Gebouw D, B-3590 Diepenbeek, Belgium

#### Abstract

Reaction mechanisms for the initial stages of naphthalene oxidation at high temperatures ( $T \ge 600$  K) have been studied theoretically [1] using density functional theory along with various exchange-correlation functionals, as well as the benchmark CBS-QB3 quantum chemical approach. These stages correspond to the removal of hydrogen atoms by hydroxyl radical and the formation thereby of 1- and 2-naphthyl radicals. Kinetic rate constants were estimated by means of transition state theory (TST). Effective rate constants have been calculated according to a steady state analysis using a two-step model:

step 1 : 
$$C_{10}H_8 + OH^{\bullet} \xrightarrow{k_1} C_{10}H_8 \cdots OH^{\bullet}$$
  
step 2 :  $C_{10}H_8 \cdots OH^{\bullet} \xrightarrow{k_2} C_{10}H_7^{\bullet} + H_2O$ 

The excellent agreement obtained with experimental kinetic rate constants demonstrates the validity of this model. Comparison with results obtained using density functional theory in conjunction with various exchange-correlation functionals also shows that DFT remains unsuited for quantitative enough insights into kinetic rate constants. Analysis of the computed structures, bond orders and free energy profiles demonstrates that the reaction steps involved in the removal of hydrogen atoms by OH radicals satisfy Leffler-Hammond's principle. Computations of branching ratios also show that this reaction does not exhibit a particularly pronounced site-selectivity.

#### Keywords

Polycyclic aromatic hydrocarbon, oxidation process, hydrogen abstraction, rate constants, transition state theory.

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<sup>\*</sup> To whom all correspondence should be addressed: +32-11-268303; E-mail: michael.deleuze@uhasselt.be (M.S. Deleuze)

### Quantum Chemical and Kinetic Study of the Oxidation Mechanisms of Naphthalene Initiated by Hydroxyl Radicals. II. The OH Addition Pathway

Abolfazl Shiroudi<sup>a</sup>, Michael S. Deleuze<sup>a,\*</sup>, Sébastien Canneaux<sup>b</sup>

<sup>*a*</sup> Center of Molecular and Materials Modelling, Hasselt University, Agoralaan, Gebouw D, B-3590 Diepenbeek, Belgium <sup>*b*</sup> Université Lille1 Sciences et Technologies, Cité scientifique, 59655 Villeneuve d'Ascq Cedex, France

#### Abstract

The oxidation mechanisms of naphthalene by OH radicals under inert (He) conditions and at temperatures smaller than 410 K (Figure 1) have been studied [1] using density functional theory (DFT) along with various exchange-correlation functionals. Comparison is made with benchmark CBS-QB3 theoretical results. Kinetic rate constants were estimated by means of transition state theory (TST) and statistical Rice-Ramsperger-Kassel-Marcus (RRKM) theory. Effective rate constants have been calculated according to a steady state analysis using a two-step model. Comparison with experiment confirms that, on the OH addition reaction pathway leading to 1-naphthol, the first bimolecular reaction step has an effective negative activation energy around -1.5 kcal mol<sup>-1</sup>, whereas this step is characterized by a positive activation energy around 1 kcal mol<sup>-1</sup> on the OH addition reaction pathway leading to 2-naphthol.



Figure 1: OH<sup>•</sup> addition upon naphthalene

The calculated branching ratios indicate that, at temperatures lower than 410 K, the most abundant product resulting from the oxidation of naphthalene by OH radicals must be 1-naphthol. The regioselectivity of the reaction decreases with increasing temperatures and decreasing pressures. The RRKM calculations demonstrate that the TST approximation breaks down at ambient pressure for the first bimolecular reaction steps. Pressures larger than 10<sup>5</sup> bar are indeed required for restoring within 5 % accuracy the validity of this approximation for all the reaction channels that are involved in the OH• addition pathway. The computed structures, bond orders and free energy profiles demonstrate that all reaction steps involved in the oxidation of naphthalene by OH radicals satisfy Leffler-Hammond's principle. Nucleus independent chemical shift indices and natural bond orbital analysis also show that the computed activation and reaction energies are largely dictated by alterations of aromaticity, and, to a lesser extent, by anomeric and hyperconjugative effects.

#### Keywords

Polycyclic aromatic hydrocarbon, oxidation process, reaction mechanisms, rate constants, transition state theory.

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<sup>\*</sup> To whom all correspondence should be addressed: +32-11-268303; E-mail: michael.deleuze@uhasselt.be (M.S. Deleuze)

### Adaptive On-the-fly Regression Tabulation: Beyond ISAT

Edward S. Blurock<sup>\*</sup> REACTION, Lund, Sweden

#### Abstract

This paper describes a tabulation method based on computing, retaining and accessing a large, on the order of millions, number of individual kinetic time step calculations and approximations. It is essentially an extension of Pope's In Situ Adaptive Tabulation (ISAT) method. The primary differences lie in that not all configurations need be stored in memory and that a polynomial approximation is only calculated when enough points have accumulated within a localized area to be able to calculate the polynomial approximation. The latter increases efficiency because no extra points are evaluated to form an approximation (as is done in ISAT). A kinetic time step can be stored as a configuration and the change (gradient) in that configuration, both n-valued vectors, or as a configuration and ndimension first order polynomial representing the gradient around that point. The individual configurations are accessed by m progress variables, temperature, pressure and selected species mass fractions, in an m-leveled tree, one progress variable per level. The values of the progress variables are divided up into a fixed number of intervals. The set of kinetics configurations at the leaf nodes of the tree are all within a hypercube of values. To maintain a reasonable memory usage, the entire database resides on disc and only the 'most used' information resides in memory. How much resides in memory can be specified, dependent on availability. For calculations over limited conditions, all configurations can reside in memory for maximum efficiency. Initial tests were made with the GRI-3.0 mechanism, with 55 species. It was found that with 9 progress variables, temperature, pressure, HO<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>, was adaquate to describe the configurations for conditions of initial temperature from 1300 to 1900 (10 degrees steps), pressure from 1 to 40 atmospheres (5 atm steps), and equivalence ratio from 0.4 to 2.0 (0.2 steps). These ranges are described by about 150000 configurations in 140000 hypercubes accessed by a tree with around 50000 nodes. The data structure is tested with the premixed pairwise mixing stirred reactor with over 100 particles.

#### Keywords

Tabulation, combustion, ISAT

#### Introduction<sup>1</sup>

Combustion systems are an integral part of the power generation and transportation industries. With the documented consequences on global warming and pollution, studying these systems to reduce pollutants and to make them more efficient is becoming an even higher priority. With the rapid and continued increase of computing power, computational fluid dynamic (CFD) computations of combustion processes from simple flames to complex engine configurations, including complex turbulence effects, is truly on par with experimental results. CFD is now not only a theoretical tool for 'explaining' phenomenon, but has become an integral part in the design process. Of increasing use and necessity are 'reactive flows' involving chemical kinetics.

One class of methods, which reduce the dependence on solving differential equation systems of, for example, reduced mechanisms (Griffiths, 1995; Tomlin and Turányi, 2013; Turányi and Tomlin, 2013). The results of solving the chemical source terms are tabulated and when accessed, have simple functional forms, usually

polynomials, or simplified kinetics (see (Blurock and Battin-Leclerc, 2013)). The results can be tabulated totally in a preprocessing step as in the 'ignition' models (Colin et al., 2005; Michel and Colin, 2014; Subramanian et al., 2007). The obvious disadvantage is that all the representative states have to be considered and calculated beforehand. Tabulations made during the CFD calculation are the (in situ) chemistry tabulation methods. In situ tabulation (ISAT) (Hedengren and Edgar, 2008; Lu and Pope, 2009; Pope, 1997; Singer et al., 2006), based on 1st degree polynomials, and Piecewise, reusable implementation of solution mapping (PRISM) (Tonse et al., 2003), based on second degree polynomials are two common methods in the literature. In the 'in situ' methods, the tabulation occurs at the same time as usage. If a state is in the tabulation, then the tabulated result is used. If the state is not in the tabulation, then a new tabulation is computed (by enough additional computations of the full problem to form a response surface). In all these methods, the entire tabulation must remain in main memory, which could put limitations on the extent of tabulation. The project work of this proposal expands upon this class of methods.

#### **Database Design**

It is assumed that a time step calculation to the solver is relatively expensive. The primary objective of the

<sup>&</sup>lt;sup>1</sup> Address correspondence to Edward Blurock, Edward.blurock@esblurock.info

design is to always reuse the results of a calculation, never have to repeat a solver calculation and not to do extra calculations. Since all calculations for the configurations are saved, a very large amount of database information has to be managed. So the basic database design has to efficiently manage and access a very large amount of data, on the order of hundreds of thousands to millions of data points. At the most primitive level, the information is a vector of elements. A significant portion of the database is not just the vector of data itself, but also the information and management data structures, a decision tree structure, needed to find the 'nearest neighbor', or point closest to the target point. Post processing techniques and play a major role in the design of this management structure. At the same time, there is always a limitation of how much data can fit into memory at one time. For efficient access, as much 'relevant' information as possible is kept in memory at one time.

Thus the database design has to balance these four principles:

- Very Large Database Every calculation is stored and kept for direct use or for post processing. As the range of conditions of the calculations expand, so does the database.
- Efficient Access The speed-up of the method is proportional to the calculation time of the solver for a time-step over the access time of the database. A significant amount of the total database structure deals with the efficient access of the nearest point. Efficient access also involves search a tree.
- Limited Memory The most efficient usage is of points within memory. Part of the database management is deciding what information should stay within main memory and which should be written to disk storage.
- **Response Approximation** The use ISAT with the first order approximation can be used to consolidate points. However, no extra calculations are done to create the approximation. An approximation is calculated only when enough points near enough each other are accumulated.
- **On- and Off-Line** The initial database can be set up through off-line calculation and then supplemented by on-line points as they are needed.

#### **Creating Zeroth Order Approximations**

The basic design of the tabulation method allows all types of approximations. However, since the database is accumulative and is meant not to produce extra calculations, a zeroeth order approximation will be used. Higher order calculations would be relevant if the number of configurations accumulated within a hypercube would be enough to warrant a, for example, polynomial approximation. Within the current algorithm, a first order approximation is made when enough distinct nearest neighbors are present to be able to calculate the approximation. However, experience has shown that the number of hyper-cubes with a sufficient number of points is few.

The accumulated information at a given configuration is the time derivative, calculated numerically using the standard time-step size (in this study, a time-step of  $10^{-5}$  seconds was used) and the difference between the initial and the final values. For the approximation, it is assumed the this gradient is constant in the region around the configuration. The response of a given point is calculated as follows:

- **Find Closest Point:** Using the progress variables the closest configuration is found (see below for a more complete explanation).
- **Time-step:** The are two cases concerning the relative value of the desired response time-step and the default time-step of the database:
  - **Greater than or equal:** In this case sub-cycling response time-step is the default (10<sup>-5</sup>). This value is subtracted from the total response time-step and cycled again.
  - **Less than:** The response is the ratio of response time-step and the default time-step.
- **Gradient**: The stored gradient times the appropriate time-step is added to the configuration to give the response configuration.

#### **Creating First Order Approximations**

For a mechanism with n species a configuration is made up of a vector with n+2 numbers. The extra two numbers are the temperature and the pressure. To create a polynomial approximation in a region n+3, i.e. one more than the dimension of the system, is needed. In the traditional ISAT algorithm, when a new configuration is needed, then a polynomial approximation is made. This means that n additional calculations have to be made. In terms of efficiency and reuse, this means that this configurations around the original point has to be used at least n times before the algorithm breaks even, i.e. before the computational gain is seen. Experiments with the method produced here indicates, that this gain is not realized. The configurations, without the approximations, can be used.

For this reason, in the method described here, these extra calculations are not done. Instead, the individual points themselves are accumulated (as described in the last section). Only when a sufficient number of distinct points, defined by that the zeroth order approximation is not accurate enough, are present is a approximation calculated. The previously used points are used to calculate the approximation. No extra calculations are made.

When the points are accumulated, the linear system is solved and an approximation is calculated. The

approximation is then checked against the original points for its validity. If the calculated approximation does not fit a few points, then these points are not considered as part of the approximation. Those that do fit the approximation are then eliminated from the hypercube.

In creating the approximation, the maximum and minimum of each parameter (meaning species mole fractions, temperature and pressure) are calculated. To determine whether the approximation should be used on a new configuration, the parameter values of the configuration has to fall within the ranges of all the parameters that were used to create the approximation.

#### **Finding Closest Point**

Tabulation methods depend on finding the closest configuration as efficiently as possible. The purpose and philosophy of the tabulation is to provide full kinetic data with computational efficiency. However, it is impractical, both for the tabulation and for the transport complexity within a CFD calculation, to use the full set of species and conditions of the full mechanism. For this reason, a reduced set of progress variables is chosen to represent the position in configuration space, i.e. the hypercube, of the calculation.

The progress variables are used to find the closest configuration. In the design of this tabulation method, this is done in two stages:

- **Hypercube:** Using a tree structure (see next section), a set of configurations bounded by a hypercube of progress variable values is isolated.
- Nearest: All configurations collected are compared and the closest (currently using the normed euclidean distance) is found. Two types of comparisons are possible:
  - **Progress Variables:** If the calculation only involves the progress variables, then only these are used. This situation occurs when the tabulated database is used by an external calculation.
  - **Full:** If the full set of variables are available, then all are used. This situation occurs when setting up the database.

#### **Tree Search for Hypercube**

As explained in the last section, a primary task of tabulation is to find, as efficiently as possible, the nearest configuration. A practical intermediate step, in lieu of linearly searching through all configurations in the database, is to narrow the search with a decision tree structure to a hypercube region encompassing a 'reasonable' set of configurations close to the target. From those configurations in the hypercube, a linear search is performed.

In this implementation, the search data structure chosen is a fixed leveled, one level per progress variable, multiple branched tree. Each non-leaf node corresponds to a progress variable. The nth progress variable is represented by the nth level in the tree, with the root node being the first level. The branches to the next node correspond to fixed intervals from a minimum to a maximum. Which branch to follow is a direct computation of which interval the value of the corresponding progress variable belongs.

The tree is built dynamically, as needed. Corresponding to the configuration, the search traverses down the levels of the tree until a leaf node is found. When a leaf node is reached, then the list of indices of the corresponding tabulations are returned.

#### **Non-Leaf Search**

At the ith, non-leaf level, the search proceeds as follows:

- **Value:** Isolate the ith progress variable from the target configuration.
- **Interval:** From the minimum, maximum and number of branches, compute which branch position, b, the value corresponds to.
- **Branch:** The index at the bth value within the node, corresponds to the node, representing the (n+1)th level, to branch to. If a node does not exist, the create an empty node of the (n+1)th level.

The computational complexity of the search with n progress variables corresponds basically to the retrieval of the n+1 nodes of the tree and then the retrieval of the set of configurations listed in the leaves. The number of nodes in the tree can be quite large, usually exceeding the number of data configurations to be indexed. Therefore, the set of nodes, are also stored in a vector that can reside both in memory and on disc.

If no configurations are found, then an expanded search is made (and, of course, the complexity increases correspondingly). The expanded search entails eliminating the constraint of the lowest progress variable. The effect is using a reduced number of progress variables. The configurations within all the leaf nodes of the sub-tree of the last considered progress variable (level of the tree) are considered as candidates to find the closest configuration. Progress variables, i.e. tree levels, are eliminated until a nonempty set of candidates is found. Using this strategy places some weight on the ordering of the progress variables used. The 'least significant' variables should be at the lower levels.

#### Interaction between memory and disc

Although it is computationally more efficient to have the entire tabulation in memory, if the computational resources do not allow this, then a reasonable possibility is to provide an interaction of memory and disc. One alternative is to rely on the general swapping mechanisms of the operating system. However, in the simplicity and generality of this approach, efficiency suffers. Another alternative is to provide a more direct tuned swapping. The method used here is to have the entire database on disc and to read into memory only that data which is called for.

The additional advantage of making use of disc storage is that with each new (CFD) calculation, the configurations of the previous calculations can be used. This is especially useful when a given mechanism is used in different configurations. The database expands as needed. This is as opposed to methods that need a pre-processing step of setting up the database before the calculation. In that case, all the anticipated configurations have to be accounted for.

If the limit of memory is reached, then the data that is 'less used', an accounting of how often the data is accessed is kept, or, usage being the same, the oldest (first in first out, FIFO).

To facilitate efficient access of the data on disc, each data point is stored on a specific fixed sized disc record on a random access data file. The data is assumed to be a fixed (maximum) size. Given a record number, basically, the position of the data point, the record is accessed directly, i.e. not searched for.

To ensure generality, the data stored in the record is not restricted to just a vector of doubles. To ensure efficiency, the data is 'encoded' into a binary form and it is this binary form that is stored on disc (often called 'serialization'). Associated with each data structure that is to be stored on disc, is a pair of routines to 'encode' the data into an efficient binary form and to 'decode' that information back into memory. These routines are also used to save and restore the total current state of the tabulation for future use and portability.

One restriction is that if a data structure is not of a fixed size, then the size of the disc record must represent the maximum size that the data point can take.

The data within memory has to be accessed efficiently in two different modes, each representing two different orderings. The first ordering is based a specific vector sequential index. The most efficient data structure for this is a vector. The second ordering is dynamic and is based on which data points should be swapped out of memory. Since this ordering is dynamic and involves frequent reordering, due to data usage, the most efficient data structure is a linked list. In order not to compromise efficiency, access to the data points in memory represented at the same time with both of these data structures. Within each respective data structure, a pointer the given data point is given. The ordering is based on two numbers:

- Access: the number of times the element (meaning the vector index) is accessed. The higher the usage, the less likely the element should be replaced.
- Age: The relative age of the object. The newer objects are replaced later (essentially, first in, last out).

Rearranging the order in the linked list involves only moving pointers within memory is that to update the linked list. The complexity of which depends on how many shifts have to be done. Since the two update operations are initialize or increment by one, the total number of shifts is limited to the number of elements having the same usage. The newest element is put at the end of the list of those having the same usage. If the number of elements in memory is large and there is even, or just single, usage of the elements, then this operation can be somewhat significant. Though definitely not as significant as disc access.

#### **Choice of Progress Variables**

The number progress variables that should be used is clearly dependent on the application and the computing environment. Considering applications in a 'normal' university environment, a 'reasonable' number of progress variables is less than 15. Currently the progress variables were chosen ad hoc, i.e. defined by the modeler. For the GRI-3.0 methane mechanism, nine progress variables gave a reasonable start (future work will concentrate on more systematic determinations of progress variables).

Two physical parameters, namely temperature and pressure, are used. Based on chemical intuition, species from the four major regions of an ignition process were chosen: Initial reactant phase, the intermediate or preignition phase, the fast ignition phase and the final products phase. The choice also reflects the use of a variety of different equivalence ratios. For the initial reactants phase, methane and oxygen were used, reflecting also the equivalence ratio. For end product phase the primary products of CO<sub>2</sub> and H<sub>2</sub>O, both taken, once again to reflect the different equivalence ratios. For the intermediate and ignition phases, several significant intermediate species and radicals were chosen. Secondary considerations are measurability and that there are representatives of both oxygenated compounds and hydrocarbons. The species chosen are  $HO_2$ ,  $H_2O_2$ ,  $CH_4$  and  $C_2H_4$ .

As explained in the section of tree search for the 'closest' value, the order of the progress variables can effect the efficiency of the search. Though the maximum and minimum values are adjusted during the tree usage, the values given were determine empirically from the range of conditions used in this study.

#### **Database Generation**

A fundamental requirement of the database is that it spans the entire set of conditions that is required for a simulation. These configurations are those within a zero dimensional adiabatic constant pressure calculation. In lieu of the (impossible, or at least impractical) task of cataloging every possible configuration, a relevant subset should be collected. The ignition process is a fairly regular process spanning a limited manifold of the entire space. This implies that collecting all the configurations that are encountered in a set of ignition (zero dimensional adiabatic constant pressure) calculations under a range of starting conditions, varying temperature, pressure and equivalence ratio, is a reasonable starting point for the tabulation.

When a collection of single ignition calculations does not cover directly is the 'mixing' of states that could be encountered within a CFD calculation due to transport. One approach to remedy this is to include in the range of starting conditions a range of mixing of the product (equilibrium) gases, the end gas residue (EGR), to the start configurations. The assumption made here is that mixing is dominated by the mixing of products and reactants. Or said another way, the flame or combustion zone, where most of the complex configurations exist, is so small or fast, that it does not contribute a significant amount to mixing. The model is essentially a two zone model.

# Mixing with Premixed Pairwise Mixed Stirred Reactor

An approach, used by Yang (Yang and Pope, 1998) to test the ISAT implementation, is the premixed pairwise mixed stirred reactor (PPMSR). This is essentially a PDF method of a set of particles is a zero dimensional stirred reactor with an inlet port of fresh premixed gas and an outlet port. A single particle represents a given configuration of temperature, pressure and species mole fractions. During a timestep, four operations are done:

- **Outlet Flow:** A set of randomly chosen particles are chosen and removed from the system representing the flow through the outlet port.
- **Inlet Flow:** An equal (to the outlet) set of particles are introduced to the system with the initial configuration, representing flow in the inlet port.
- **Pairwise Mixing:** A subset of pairs of particles (how many depends on simulation parameters, see below) are randomly chosen and their configurations mixed.
- Advance: Each particle is allowed to advance a timestep in a zero dimensional adiabatic constant pressure calculation.

#### Methane Mechanism: GRI 3.0

With the residence times given, with 200 particles, four particles, or two pairs, are involved in mixing and four particles flow in and out of the total set of particles per time step. This produces a suitable amount of mixing terms. The particles are chosen randomly and thus the type of particles that mix is dependent on the percentage of particles of each phase of the calculation.

Temperature	1300-1900 in 10 degree increments
Pressure	1 atm, and 5-40 in 5 atm increments
Equivalence Ratio	0.4-2.0 in 0.2 increments

Table : The range of conditions used for the full tabulation of the 'standard' database.

#### Timings

The total timing per cycle is influenced by basically three factors:

- **In Memory** If the indexing nodes and configuration is already in memory, the retrieval is the most efficient.
- **From Disk** If some or all of the indexing nodes have to be retrieved from disk, the retrieval time is dominated by the disk access time.
- No Point on Node If the final indexed node does not have a corresponding configuration point, then the configurations and nodes from the next level must be accessed. This increases the number of nodes to be retrieved.

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### FAST PYROLYSIS OF LIGNOCELLULOSIC BIOMASS: DESIGN AND CONSTRUCTION OF A MICRO-PYROLYSIS SETUP FOR INTRINSIC KINETIC MEASUREMENTS

Hilal Ezgi Toraman<sup>\*</sup>, Hans-Heinrich Carstensen, Kevin M. Van Geem and Guy B. Marin Laboratory for Chemical Technology, Ghent University Technologiepark 914 B-9052, Ghent

Keywords

Fast pyrolysis, lignocellulosic biomass, intrinsic kinetics.

Depleting oil resources, growing environmental concerns and increasing energy demands have forced researchers to investigate biomass as a renewable, abundant and comparably cleaner alternative to fossil resources. Biomass fast pyrolysis has proven to be a promising, clean and renewable production process. The main constituents of biomass are lignin, cellulose and hemicellulose and the term "biomass" is used to refer to all organic materials that come from plants, trees, crops, and algae. During fast pyrolysis, biomass is rapidly heated yielding gaseous products, liquids (bio-oil and water) and solid charcoal<sup>1</sup>. Until recently, the main objective of this process was on converting as much of the biomass as possible to oil. However, it is crucial to pay attention to the solid biomass to gas/liquid reactions that occur prior to the complex series of secondary reactions in order to develop a mechanistic understanding of the pyrolysis pathways. For this reason, a unique micro-pyrolysis reactor setup, which is a rapidly heated two-stage isothermal pyrolysis reactor, has been designed and constructed for the experimental investigation of biomass fast-pyrolysis. The new micro-pyrolysis setup allows performing a broad set of experiments for the investigation of primary fast pyrolysis products, i.e. solid biomass to gas/liquid conversion products as a function of various parameters such as temperature (300-900°C), carrier gas flow rate (100-500 ml/min), sample size (200-1000 µg) and reactor feed composition, i.e. well-chosen model compounds for cellulose, hemicellulose and lignin. A detailed analysis of the experimental data can be obtained using a combination of advanced techniques such as comprehensive two dimensional gas chromatography (GC×GC) with on-line detectors such as flame ionization detector (FID) and time-off-flight mass spectrometer (TOF-MS). Moreover, the micro-pyrolysis setup enables us to obtain intrinsic pyrolysis kinetics at different pyrolysis temperatures by coupling the first reactor directly to the time-resolved analytics, i.e. TOF-MS. It is also aimed to work at low ionization energies ("soft" electron ionization) in order to enhance structural elucidation via less fragmentation. Based on the experimental data and chemical insights a detailed mechanism can be constructed for the solid biomass to gas/liquid conversion process.

#### Acknowledgements

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### KINETIC AND THERMODYNAMIC STUDIES OF CADMIUM REMOVAL BY ADSORPTION ON NATURAL BROWN CLAY

Latifa Bentchikou<sup>a,\*</sup>, Abdelhamid Mellah<sup>b</sup>

<sup>a</sup> Ecole Nationale Supérieure des Sciences de la Mer et de l'Aménagement du Littoral, B.P.19 Bois des Cars, Campus Universitaire, Dely-Ibrahim, Algiers, Algeria

<sup>b</sup>Centre de Recherche Nucléaire d'Alger, 2 Bd. Frantz Fanon B.P.399 Algiers, Algeria

Keywords

Removal, adsorption, cadmium, natural Ghassoul clay, kinetic, thermodynamic.

The present study investigates the removal of cadmium from aqueous solution, by natural Algerian brown clay, called locally Ghassoul, in batch mode, at different temperatures.

Kinetic experiment showed that the adsorption process can be simulated by pseudo-second order model.

In order to determine the best-fit-isotherm, the experimental data were analyzed by the Freundlich, Langmuir, Temkin and Dubinin-Radushkevich equation, at different temperatures of 293, 303, 313 and 323K. The mean deviation obtained from the four models revealed that Langmuir is the most suitable one.

Thermodynamic parameters were evaluated. The positive values of  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  reflected respectively the endothermic nature and the affinity of the adsorbent material towards cadmium. The negative values obtained of change in Gibbs free energy ( $\Delta G^{\circ}$ ) indicate the feasibility and spontaneous character of the process.

### AN EXPERIMENTAL AND THEORETICAL STUDY OF CYCLOPENTADIENE-ETHENE CO-PYROLYSIS: GROWTH OF POLYCYCLIC AROMATIC HYDROCARBONS

Marko R. Djokic<sup>a</sup>, Aäron G. Vandeputte<sup>b</sup>, Shamel S. Merchant<sup>b</sup>, William H. Green<sup>b</sup>, Kevin M. Van Geem<sup>a</sup>, and Guy B. Marin<sup>a</sup>

<sup>a</sup>Laboratory for Chemical Technology, Ghent University, Technologiepark 914, 9052 Gent, Belgium <sup>b</sup>Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA

#### Keywords

1,3-Cyclopentadiene, PAHs formation, co-pyrolysis, kinetic modeling

#### Abstract

The present contribution drastically improves fundamental understanding of polycyclic aromatic hydrocarbons (PAHs) growth using both experimental and ab-initio calculations. Co-pyrolysis experiments of 1,3-cyclopentadiene (CPD) and ethene were studied in a tubular continuous flow reactor at a fixed pressure of 1.7 bara and a dilution of 1 mol CPD / 1 mol ethene / 10 mol N<sub>2</sub>. The temperature was varied between 873 and 1163 K resulting in CPD conversions between 1 and 96% and total PAHs formation between 1 and 80 wt%. Using an automated reaction network generator, RMG, a single-event microkinetic model that captures the initial formation of indene and naphthalene from CPD is generated. Parameters requiring refinement are identified through sensitivity analysis of the RMG prediction and by comparison to experimental data. These parameters are not "fitted" to the data; but the individual reactions are subjected to an increased level of theoretical analysis or direct experimental measurement. The resulting, more accurate parameters are then added to the RMG database of chemistry rate rules to improve future model predictions for both the current fuel molecules and other similar molecules. Thermodynamic and kinetic data of sensitive species and reactions were calculated using quantum chemistry calculations at the CBS-QB3 level. Fig. 1 shows the comparisons between experimental results and model predictions of the main reaction products during co-pyrolysis of CPD and ethene at different reactor temperatures, confirming the good agreement between experiments and simulations.



**Fig. 1:** Model predictions (full lines) vs. experimental measurements (symbols) of the main reaction products during the co-pyrolysis of CPD and ethene (1.7 bara, dilution of 1 mol CPD/ 1 mol ethene/ 10 mol  $N_2$ ,  $F_{0,CPD} = 13.6$  mg/s).

### Understanding the decomposition of sulfur compounds during steam cracking and their influence on coke formation and product distribution

Natalia Olahova<sup>\*</sup>, Marko R. Djokic, Stamatis A. Sarris, Ruben Van de Vijver, Marie-Françoise Reyniers, Kevin M. Van Geem and Guy B. Marin

Laboratory for Chemical Technology, Ghent University, Technologiepark 914, 9052 Ghent,

Belgium

Keywords

Steam cracking, coke formation, sulfur components, kinetic modeling

The production of light olefins (i.e. ethene, propene and butadiene) and aromatics (i.e. benzene, toluene and xylenes) by steam cracking of hydrocarbons is one of the most energy-consuming processes of the chemical industry. <sup>1</sup> The formation of coke on the inner wall of the tubular reactors through secondary reactions has a deleterious effect on the process energy efficiency. Eventually the formed coke reduces the cross-sectional flow area of the tube, thus increasing the pressure drop and inhibiting heat transfer from the tube to the process gas. To main the same conversion the external tube wall temperature needs to be increased. Thereupon cracking yields are lowered which has an adverse impact on the economics of the process. <sup>2</sup> In light of these energy and economic drawbacks many efforts have been made towards the development of effective technologies to reduce coke formation.

In the present work, the focus is on the most widely applied anti-coking technique in industry, the application of sulfur-based additives. It is well proven that sulfur-based components, either present in the feed or used as additive, influence coke formation during steam cracking. However, so far there is very limited fundamental understanding how these components react under typical industrial conditions. In general there is agreement about their capacity on diminishing the CO production by passivating active nickel sites of the cracking coil material <sup>3</sup>, but the effect on the rate of coke formation still remains complex and debatable. In the present contribution new insight on the role of sulfur components during steam cracking process has been obtained. Several sulfur-based additives have been experimentally tested under a variety of process conditions. Next, a novel automated mechanism generation code Genesys<sup>4</sup> has been used in order to generate a kinetic model for the decomposition of sulfur-containing components. Finally, the constructed model was employed to assess the acquired experimental data.

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# Reactions of the simplest Criegee intermediate studied directly using a novel multipass, broadband time-resolved absorption spectrometer

#### Thomas R. Lewis<sup>\*</sup>, Mark A. Blitz and Dwayne E. Heard University of Leeds Leeds LS2 9JT

Criegee Intermediates (CIs), formed from the Ozonolysis of alkenes in the atmosphere have generated significant interest in the Atmospheric Chemistry community. Ozonolysis is one of the primary pathways for the removal of alkenes in the troposphere, and so the formation and subsequent removal of CIs is important for understanding the fates of unsaturated VOC emissions. Taatjes et. al discovered a method of reliably making CIs in laboratory-based experiments by photolysing di-iodo alkanes in the presence of oxygen, facilitating kinetic and spectroscopic studies of these intermediates. Absorption spectroscopy has proven particularly useful for studying CIs, and outlined here is the first body of work done using a novel new broadband, time resolved absorption technique, capable of measuring absorption between 250-850 nm simultaneously, with millisecond time resolution. Perhaps most notable of these studies is the direct observation of the reaction of CIs with water dimer<sup>1</sup> (specifically the simplest CI – CH<sub>2</sub>OO), which will dominate CI removal in the atmosphere, a result in agreement with a recent study by Lin et.al<sup>2</sup>. The efficacy of this new instrument for probing reactions of CIs has been demonstrated further through the direct observation of the reaction between the simplest CI and NO<sub>2</sub>; a reaction which was reported to yield NO<sub>3</sub>.<sup>3</sup> NO<sub>3</sub> was not observed to be a product of the reaction between the simplest CI and NO<sub>2</sub>, and can be confidently dismissed based on the data acquired due to the ability of this new absorption system to measure absorption from the UV (CI) all the way to the near IR, where NO<sub>3</sub> absorbs strongly. The reaction

The features of this new absorption system are the long path length (in excess of 10m overlap with an excimer beam), and high light throughput to the CCD chip, which facilitates the remarkable sensitivity demonstrated by the instrument, which has demonstrated the ability to measure time-resolved absorptions of less than 0.0005. The mirror arrangement is such that the overlap between the broadband probing light from a Laser Driven Light Source (LDLS) or Xe-Arc lamp and an excimer pulse at 248nm is maximized, providing an efficient way of obtaining signal whilst minimizing losses in probe intensity.

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### A NEW GROUP ADDITIVE KINETIC MODEL FOR PYROLYSIS OF C2-C4 HYDROCARBONS

Muralikrishna Khandavilli, Kevin M. Van Geem<sup>\*</sup>, Ruben Van de Vijver and Guy B. Marin Laboratory for Chemical Technology University of Gent, Gent Technologiepark 918 B-9052, Zwijnaarde, Belgium

#### Abstract

A detailed kinetic model of elementary reactions was developed to predict the product yields in steam cracking of C2 - C4 alkanes. The kinetics and thermodynamic properties were derived from a consistent set of ab-initio derived group additive values (GAV). The kinetic model consists of 556 reversible reactions between 136 species. The model was generated using the in-house automatic mechanism generator code "Genesys". The model predictions were compared with new experimental data generated for pure or rich-single alkane feeds consisting of – ethane, propane and isobutane. The Group Additive model performance was compared with popular models – JetSurF 2.0, AramcoMech 1.3, POLIMI and one generated with RMG. Based on the agreement between simulated and experimental product yields, it was found that the Group Additive model gave the best performance without adjusting any of the ab-initio derived GAV's. Rate and sensitivity analysis is used to identify the most important reactions and differences in rate coefficient assignments in the models.

#### Keywords

Steam Cracking, Pyrolysis, Group Additivity, Kinetic Modeling

#### Introduction

Steam cracking is the most commercially viable route to form important lower olefins like ethylene, propylene and butadiene [Van Geem et al]. These lower olefins are in turn raw materials for important polymers. Typical feedstocks of steam cracking range from light gases such as ethane to highboiling distillates from oil refining. Typical cracking temperatures are in the range of 700 °C to 900 °C, the pressure is 0.15 - 0.35 MPa and residences times vary from 0.1 - 1 s. This article focuses on steam cracking of light alkanes - ethane, propane and isobutane. Experimental data was obtained from an in-house pilot plant [Sabbe et al., AIChE]. The products analyzed were hydrogen, methane, ethane, ethylene, propane, propylene, n-butane, isobutane, isobutene, n-butenes, acetylene, methyl acetylene/ propadiene, 1,3cyclopentadiene, 1,3-butadiene, benzene.

Due to the large throughputs employed in the steam cracking industry, any improvement in process conditions or change of feedstock can lead to a huge economic impact [Speight]. Hence, for knowledge driven improvements, a good fundamental understanding of the steam cracking process is a must. \* To whom all correspondence should be addressed

This includes the mechanistic understanding of the gas phase pyrolysis chemistry, which is known to be dominated by radical reactions such as bond fissions, hydrogen abstraction, additions to multiple bonds and the corresponding reverse reactions. Typically such radical mechanism consists of hundreds of species involved in thousands of elementary reactions. As it is not feasible to determine the thermodynamics and kinetics of so many species and radical reactions experimentally, estimation procedures are usually used. Several kinetics estimation procedures have been developed which are based on the structure of the transition state such as the structural group contribution method [Willems and Froment - 2 articles], the supergroup thermochemistry for transition states [Sumathi, Carstensen and Green - 3 articles] and the reaction class transition state theory [Truong - 2 articles]. Another modeling route is the group additive method for activation energy and pre-exponential factor [Sabbe et al.- 3 articles, Saeys et al. - 1 article]. Sabbe's work has shown that the group additive kinetics methodology gives the closest approximation to an ab-initio kinetic rate coefficient as applied to the transition state theory. A maximum factor of 4 can be expected by this methodology, while density functional theory (DFT) may give rise to a rate coefficient which is a factor of 10 different from ab-initio. Since ab-initio calculations for all the reactions would prove to be too expensive, the group additive approach is applied as an approximation and for on-the-fly calculation of rate coefficients during an automatic network generation procedure using the in-house code "Genesys", as shown in the article by Van de Wiele et al. The present study has used Genesys to automatically generate the group additive model and the predictions have been compared with experimental data and other popular models predictions.

#### Automated mechanism generation and validation

Genesys [Van de Wiele et al.] was used to generate the kinetic model for steam cracking of ethane, propane, n-butane and iso-butane feeds. In this methodology, the feed molecules are made to undergo reactions as per those specified in the reaction family database. Subsequent species formed are added to the species list and reactions to the reactions list while observing a few constraints specified by the user. The constraints used here were the species size kept at a maximum carbon number of 6. Kinetic parameters for the reactions generated are assigned from the kinetics Group Additive Values ( $\Delta GAV^{\circ}$ ) databases, hence generating the consistent kinetic model (GA model). Thermodynamics of species are calculated with the CBS-QB3 method [Sabbe et al, AIChE]. The reaction families considered were addition reactions by H atom and carbon centered radical addition across an unsaturated bond, hydrogen abstractions by H atom and carbon centered radical, radical recombination reactions, and their reverse families. The kinetic model generated contains 556 reactions among 136 species. The model was compared separately for steam cracking of ethane, propane and isobutane. Experimental data was available from an in-house pilot plant. The simulation was done in ChemKin [ChemKin, 10131], the reactor model being Plug Flow reactor. The temperature and pressure profiles were readily known from pilot plant data and were used in simulation. The pilot plant has a tube diameter of 1 cm and a total tube length of 23.13 meters. Gas temperatures were measured at 23 different points. Residence times were in the range of 0.3 - 1.5 s. The pressure was between 1.5 and 3 atm.

The GA model performance for various products was then compared with existing popular models – JetSurF 2.0 [Wang et al.], AramcoMech 1.3 [Metcalfe et al.], Ranzi model of POLIMI [Ranzi et al.] and that generated by RMG [Green et al.]. The comparison was made by visual inspection of parity plots of experimental versus predicted weight% of a particular product.

Results

First, ethane cracking was simulated with the 556 reactions GA model and the results matched those by the 1512 reactions, 129 species model by Sabbe et al. (AIChE). Principal Component Analysis [Vajda et al.] was used to find a shortlist of 42 dominant reactions and 28 dominant species from GA model for ethane cracking. According to this, the most dominant hydrogen abstraction reactions are those by hydrogen atom and methyl radical on ethane molecule giving ethyl radical. Ethane C-C scission giving two methyl groups and C-H scission giving an ethyl radical are dominant initiation mechanisms, while hydrogen addition to ethylene is a dominant addition mechanism. The 556 reaction model provides for formation of benzene and cyclopentadiene, but their yields for the particular validation data set used is negligible.

The ethane cracking experimental data set was compared with model predictions of GA, JetSurF, Aramco, Ranzi and RMG. This was done for four main products – H2, CH4, C2H4 and conversion of ethane (1 parity plot for each product per feed set). This procedure was repeated for propane feed and isobutane feed. Sample parity plots are shown in figures 1 and 2.

Figure 1 shows the parity plot of ethylene product for ethane cracking. As can be observed, the JetSurF model gives the best performance. The GA model systematically overpredicts the ethylene yields while the Aramco and Ranzi mechanisms lead to severe under-predictions. The feed ethane conversion is also overpredicted by the GA model and underpredicted by Ranzi and Aramco mechanisms, while the JetSurF model reproduces the conversion well. For methane yield predictions, RMG gives the best results, while all other models under-predict it. The GA and lead Aramco models to the most severe underpredictions. Hydrogen yield predictions have a much narrower spread though the GA model overpredicts it compared to other models.



Figure 1. Ethylene product from Ethane cracking

The predictions of the GA model are better compared to other models when it comes to propane and isobutane cracking. Figure 2 shows the parity plot of propylene yields from isobutane cracking. As can be observed, the GA and RMG models lead to the best predictions, while JetSurF predicts too low and Aramco too high propylene yields. For ethylene yields, models JetSurF and RMG lead to maior underpredictions and the Ranzi also model underpredicts it. Here, too, the GA model performs best, closely followed by the Aramco model. Hydrogen and methane yields show a comparatively narrower spread. The GA model gives the best results in these too, while JetSurF and Ranzi deviate most from the experimental data. Isobutane conversion is predicted best by Aramco closely followed by GA. JetSurF shows large underprediction for isobutane conversion, while for isobutene product, it is the best and all other models deviate from the parity line.



Figure 2. Propylene product from Isobutane cracking

Table 1 lists the feed, major cracking products and the model that provides the best prediction for each product. It can be seen that the GA model scores better in most categories, as summarized in table 2

Table 1.	Comparison of kinetic models for ethane,
	propane, isobutane cracking

Feed	Major product	Best model
Ethane	Conversion	JetSurF
	Ethylene	JetSurF
	H2	Ranzi
	CH4	RMG
Propane	Conversion	Aramco
	Ethylene	Aramco
	H2	GA
	CH4	Aramco
	Propylene	GA
	Ethane	GA
Isobutane	Conversion	Aramco
	Isobutene	JetSurF
	Ethylene	GA
	Propylene	GA
	H2	GA
	CH4	GA

Table 2. Number of product plots for best trends

Model	Best trends for products
GA	7
JetSurF	3
Aramco	4
Ranzi	1
RMG	1

#### Conclusions

A new automated mechanism generation tool, Genesys, has been employed to build a kinetic model for steam cracking of ethane, propane and isobutane. The group additive (GA) model is completely based on elementary step reactions with rate expressions assignments based on group additivity. The final mechanism contains 136 species and 556 reactions. Predictions of this mechanism for ethane steam cracking is acceptable while for the fuels propane and isobutane good agreements between predicted and observed product yields was found. No adjustments of rate parameters were made to improve the predictions because the goal of this study was to explore the state of the art of generic kinetic models. Comparison with kinetic models found in literature revealed that the Aramco mechanism is of similar quality, the other models agree less with the experimental data than the GA model.

#### Acknowledgments

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### THE SPIN-FORBIDDEN REACTION OF ATOMIC SULFUR WITH ETHYLENE

Kristopher M. Thompson, Yide Gao and Paul Marshall\* University of North Texas Denton, TX 76203

#### Abstract

Ground-state S-atoms were generated by pulsed laser photolysis of OCS precursor, and monitored by timeresolved resonance fluorescence. The kinetics were studied over the temperature range of 291 - 1052 K. Below 800 K the effective bimolecular rate constant *k* was found to be independent of pressure, and also to be in good accord with prior measurements made at 442 K and below. At higher temperatures, pressure fall-off curves were characterized. These demonstrate that the reaction is dominated by addition without fast fragmentation of the resulting adduct(s). Extrapolation via the Troe formalism yields the high-pressure limit, which along with the lower temperature data may be summarized as

 $k = 1.4 \text{ x } 10^{-11} \exp(-8.3 \text{ kJ mol}^{-1}/\text{RT}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (T} = 291-1052 \text{ K})$ 

The low-pressure limiting rate constant is also obtained. The observation of formation of one or more adducts even at  $\sim 1000$  K constrains their thermochemistry, and comparison with the computed reaction enthalpies for various candidates in the literature shows that the addition process must be spin-forbidden. We characterize the triplet-singlet curve crossing with *ab initio* methods.

#### Keywords

S atom, ethylene, reaction rates, intersystem crossing, RRKM theory

#### Introduction

The interactions between sulfur and hydrocarbon species are important parts of the Claus process to separate sulfur from fuels, and understanding the mechanism may assist mitigation of undesirable side products. Here we present new measurements on the  $S + C_2H_4$  system, which has also been discussed in the context of astrochemistry.

Previous measurements of the second-order rate constant  $k_1$  for reaction

$$S + C_2H_4 \rightarrow \text{products}$$
 (1)

did not reveal any dependence on the pressure of the bath gas M, with M typically N<sub>2</sub> or Ar (Donovan et al., 1970, Connor et al., 1971, Strausz et al., 1971, Davis et al. 1972). This is consistent with either an abstraction mechanism or an addition mechanism at the highpressure limit. We made measurements over wide ranges of temperature and pressure to distinguish between these possibilities, via the first observation of pressure falloff in  $k_1$ . There have also been *ab initio* computational studies of reaction (1) and these are used to help interpret the observations (Woon, 2007, Leonori et al., 2009). • To whom all correspondence should be addressed

#### Methodology

Ground state atomic sulfur atoms were generated by pulsed laser photolysis of OCS precursor at 248 nm, and monitored by time-resolved resonance fluorescence in the vacuum UV. Details have been provided elsewhere (Ayling et al., 2015). In brief, mixtures of OCS and C<sub>2</sub>H<sub>4</sub> in a large excess of argon bath gas are photolyzed. The concentration of S atoms follows pseudo-first-order kinetics and plots of the decay constant vs. [C<sub>2</sub>H<sub>4</sub>] yield the effective secondorder rate constant  $k_1$ .

#### Results

51 determinations of  $k_1$  over 291 - 1052 K were made. No significant variation of  $k_1$  with experimental parameters such as the laser photolysis energy, the OCS concentration or the residence time inside the heated reaction cell was observed, consistent with successful isolation of the elementary reaction (1) from potential secondary chemistry involving photolysis or reaction products.

There is good accord between our data and literature values (Davis, et al., 1972) at about 290 and 450 K. Below 800 K we confirm the absence of an observed dependence on pressure, but at about 950 and

1050 clear falloff curves were obtained. Fitting to the Troe formalism yields the low- and high-pressure limit rate constants  $k_{I,0}$  and  $k_{I,\infty}$ , respectively. An Arrhenius plot of the high-pressure limit is shown below, which yields the rate expression

 $k_{I,\infty} = 1.4 \text{ x } 10^{-11} \text{ exp}(-8.3 \text{ kJ mol}^{-1}/\text{RT}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 

 $k_{1,0}$  is ca. 2 x 10<sup>-28</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> around 1000 K.

Figure 1. Arrhenius plot for the high-pressure limit of  $S + C_2H_4$ . Open circles: pressure independent data. Half-filled circles: obtained from extrapolation of falloff curve.

#### Discussion

The presence of a pressure falloff reveals that the mechanism involves stabilization of an initially excited adduct, which must be stable at 1052 K. This means the binding energy must be at least 150 kJ mol<sup>-1</sup>. Comparison with the *ab initio* analysis of Leonori et al. (2009) indicates that triplet adducts are bound by at most 5 kJ mol<sup>-1</sup> and may be ruled out. Singlet species with sufficient stability are thiirane (a three-membered ring with S bonded across the carbon atoms), ethenethiol and thioacetaldeyde, all ca. 250 kJ mol-1 below the reactants. Reaction (1) is therefore spinforbidden. The potential energy diagram suggests that thiiirane is the initial product, while the bottleneck to the other two species is a barrier at the same height as the triplet reactants. At the high-pressure limit we therefore expect the dominant product is thiirane.

The rate constant for the spin-allowed removal of S(<sup>1</sup>D) by C<sub>2</sub>H<sub>4</sub> is ca. 4 x 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Leonori, et al., 2009) and so the Arrhenius A factor for  $k_{I,\infty}$  can be rationalized with a probability for intersystem crossing (ISC) of 0.035. Using density functional theory, B3LYP/cc-pV(T+d)Z, we have optimized an intersystem crossing point for addition of S to C<sub>2</sub>H<sub>4</sub> perpendicular to the  $\pi$  bond which lies ca. 3 kJ mol<sup>-1</sup> above the triplet reactants. The computed S-C distance here is 2.63 x 10<sup>-10</sup> m. Other geometries may also play a role; the conclusion here is that the barrier to ISC is small and broadly consistent with the observed activation energy.

#### Conclusions

The kinetics for S addition to ethylene have been observed at up to 1052 K. The results are consistent with spin-forbidden thiirane formation.

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### GAS-PHASE REACTIVITY STUDY OF C<sub>3</sub>F<sub>7</sub>CH=CH<sub>2</sub> WITH OH RADICALS, CI ATOMS AND OZONE

Amparo Soto<sup>\*1</sup>, Bernabé Ballesteros<sup>1,2</sup>, Elena Jiménez<sup>2</sup>, Alberto Moreno<sup>1</sup>, Sergio González<sup>2</sup>, José Albaladejo<sup>1,2.</sup> <sup>1</sup>Universidad de Castilla-La Mancha – Instituto de Combustión y Contaminación. Ciudad Real, 13071 Spain <sup>2</sup>Universidad de Castilla-La Mancha – Departamento de Química Física - Facultad de Ciencias y Tecnologías Químicas. Ciudad Real, 13071 Spain

#### Abstract

Perfluorinated carboxylic acids (PFCAs) have shown to be bioaccumulative and potentially toxic. There are no known natural sources of PFCAs, these compounds have been directly emitted to the environment via industrial processes. A portion of the observed PFCAs may originate from precursor substances, which are transformed by atmospheric oxidation processes such as reaction of hydrofluoroolefins with main tropospheric radicals (OH, Cl and O<sub>3</sub>). Therefore, our study of the atmospheric chemistry of  $C_3F_7CH=CH_2$ reports the rate coefficients for these reactions, the lifetime of this species and the products formed in the absence of NO<sub>x</sub>. In addition, the ability of  $C_3F_7CH=CH_2$  to survive long-range transport hence potentially contributing to global burden of PFCAs formed in the investigated reactions is evaluated in this work.

#### Keywords

Hydrofluoroolefins (HFOs), Rate coefficients, Products, Perfluorinated carboxylic acids (PFCAs), Atmospheric chemistry

#### Introduction

Hydrofluorocarbons (HFCs), second generation of CFC substitutes, are already covered by the United Nations Framework Convention on Climate Change (UNFCCC) and its Kyoto Protocol. HFCs have zero ozone depleting potential, but they significantly contribute to the greenhouse effect because of the presence of IR absorbing C-F bonds. Developing countries are phasing out high global warming potential (GWP) HFCs and moving to lower GWP alternatives. Hydrofluoroolefins (HFOs) are currently under consideration as viable HFC alternatives for a number of applications. Another problem is the production of Perfluorinated Carboxylic Acids (PFCAs) by atmospheric oxidation process of HFCs. PFCAs have been shown to be bioaccumulative and potentially toxic. Human and animal tissues collected in urban and remote global locations contain these compounds (Martin et al., 2003; Berthiaume et al., 2002; Biegel et al., 2001; Dupont ®).

Absolute and relative kinetic techniques have been used to determine the rate coefficients for the reaction of  $C_3F_7CH=CH_2$  (HFO) with the main oxidants in the troposphere, i.e. OH radicals, Cl atoms and ozone. The Pulsed Laser Photolysis-Laser Induced Fluorescence (PLP-LIF) technique has been used for the absolute kinetic study with OH radicals between 263 K and 358 K and as a function of total pressure (50-650 Torr). \*Amparo.Soto@uclm.es; Bernabe.Ballesteros@uclm.es

Atmospheric simulation chambers has been utilized for both kinetic and products study of Cl and  $O_3$  reactions at 298K  $\pm$  2K and 720  $\pm$  5 Torr of pressure in air. Fourier Transform Infrared (FTIR) spectroscopy and Gas Chromatography – Mass Spectrometry/ Solid-Phase Microextraction (GC-MS/SPME) technique were employed as detection techniques.

#### **Experimental Set-Up**

The **absolute kinetic** measurements of reactions with OH radicals were performed by pulsed laser photolysis (PLP) coupled to the laser induced fluorescence (LIF) technique (Antiñolo et al., 2011).

The temperature in the jacketed Pyrex reactor is measured by a movable thermocouple inserted just above the reaction zone inside the reaction cell. Total pressure in this small Pyrex reactor usually is varied from 50 to 650 Torr of He (the buffer gas). Gases are introduced in the reactor by means of mass flow controllers of different flow rates. The pulsed (10 Hz) laser photolysis of a precursor (H<sub>2</sub>O<sub>2</sub> or HNO<sub>3</sub>) was used to generate in situ OH radicals in the electronic ground state, X<sup>2</sup>II. Photolysis radiation was provided by a KrF excimer laser. The generated OH radicals were excited at 282 nm (X<sup>2</sup>II v''=0  $\rightarrow$ A<sup>2</sup> $\Sigma$ <sup>+</sup>, v'=1).The excitation frequency was obtained by doubling the output radiation from a dye laser pumped by a NdYAG. Off-resonance fluorescence (most intense band around 308 nm,  $A^2\Sigma^+$ ,  $v' = 0 \rightarrow X^2\Pi$ , v'' = 0) was detected by a filtered photomultiplier tube. Temporal profiles of the LIF signal from OH radicals (I<sub>LIF</sub>) were recorded as a function of the reaction time given by the delay between the probe and photolysis lasers. From the analysis of such decays, the pseudo-first order rate coefficients are derived at a given reactant concentration.

The overall loss of OH radicals is due to the following processes:

$OH + C_3F_7CH = CH_2 \rightarrow Products$	kон	(1)
$OH \rightarrow Other \ losses$	$k_0$	(2)

Under pseudo-first order conditions:

$$[OH(X^{2}\Pi)]_{t} = [OH(X^{2}\Pi)]_{0}exp(-k't)$$
  
$$k' = k_{OH}[C_{3}F_{7}CH=CH_{2}] + k_{0}$$

In the study with Cl and  $O_3$  a relative technique was employed using two environmental equipped with FTIR and GC-MS chambers (Ballesteros et al., 2009). The first one consists of a multipass 16 L borosilicate glass cylinder reaction chamber coupled to a Nexus Thermo Nicolet FTIR spectrometer. The second one consists of a 264 L environmental reactor, where gas samples were analyzed by a GC (Thermo Electron Co., model Trace GC Ultra) coupled to a Mass Spectrometer (Thermo Electron Co., model DQS II). Ozone was generated from O<sub>2</sub> via silent electrical discharge using a commercial ozonizer (OZOGAS T.R.C.E.- 5000), and chlorine atoms were generated by continuous UV photolysis of Cl<sub>2</sub>.

In the relative rate experiments, the following reactions take place:

$$X + \text{HFO} \rightarrow \text{products} \qquad k_{HFO} \qquad (3)$$
$$X + R \rightarrow \text{products} \qquad k_R \qquad (4)$$

where X = Cl or  $O_3$  and R = reference compound. It can be shown that:

$$\ln\left(\frac{[HFO]_0}{[HFO]_t} - (k_w)t\right) = \frac{k_{HFO}}{k_R}\ln\left(\frac{[R]_0}{[R]_t} - (k'_w)t\right)$$

where  $[HFO]_0$ ,  $[R]_0$ , [HFO]t, and [R]t are the concentrations of reactant and reference at time  $t_0$  and t,  $k_{HFO}$  and  $k_R$  are the rate constants for the reactant and the reference, and  $k_w$  and  $k'_w$  is the rate coefficient for wall loss of the reactants and reference compounds. Plots of

 $ln\left(\frac{[HFO]_0}{[HFO]_t}\right)$  vs.  $ln\left(\frac{[R]_0}{[R]_t}\right)$  should be linear, passing through the origin and with a slope equal to  $\frac{k_{HFO}}{k_R}$ .

#### Results

**1.Study of the kinetics of C<sub>3</sub>F<sub>7</sub>CH=CH<sub>2</sub> with OH radicals as a function of pressure and temperature. Absolute Technique** 

Figure 1 shows that the rate coefficients  $k_{OH}$  at 298K were observed to be independent on total pressure between 50 and 650 Torr. The average value of  $k_{OH}$  is reported to be  $(1.24\pm0.18)\times10^{-12}$  cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup>. Assuming an average OH concentration of 10<sup>6</sup> radicals cm<sup>-3</sup> (Prinn et al., 2001) in the atmosphere, the lifetime is estimated to be 9 days.

On the other hand, it has been observed dependence of the rate constants with temperature, so that the following Arrhenius expression is obtained:

 $k_{\rm OH} = (7.36 \pm 0.40) \times 10^{-13} \exp\{(161 \pm 16)/T\}$ cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup>.



**Figure 1**. Representation of  $k' - k_0$  vs.  $[C_3F_7CH=CH_2]$  at 298 K and a different total pressures in the range 50-650 Torr

## 2. Kinetics of C<sub>3</sub>F<sub>7</sub>CH=CH<sub>2</sub> with Cl atoms and O<sub>3</sub>. Relative Technique.

FTIR technique was employed as a detection method of  $C_3F_7CH=CH_2$  and the reference compound. Figures 2 and 3 show relative rate data for the reaction of  $C_3F_7CH=CH_2$  with Cl and O<sub>3</sub>. Reference compound used for studying the ozone reaction was acrolein ( $k=3.01\times10^{-19}$  cm<sup>3</sup>molecule<sup>-1</sup> s<sup>-1</sup>, Treacy, et al., 1992)) while propane ( $k=2.23\times10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, Ceacero et al., 2009) and 1,3-butadiene ( $k=4.20\times10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, (Ragains et al., 1997) were used as reference compounds in the Cl-reaction.



**Figure 2**. Relative rate data for the reaction with Cl using propene and 1,3-butadiene as reference compound.



**Figure 3**. Relative rate data for the reaction with O<sub>3</sub> using acrolein as reference compound

Table 1 shows the rate constants for the studied reactions. There is a big difference in the reactivity of the compound under study with different tropospheric oxidants at (298±2)K and 720Torr, reacting much faster with Cl atoms compared with ozone and OH radicals. The tropospheric life times of C<sub>3</sub>F<sub>7</sub>CH=CH<sub>2</sub> shown in Table 1 have been calculated with respect to O<sub>3</sub>, Cl and OH reactions, using the rate coefficients at room temperature and taking into account the following concentrations (in units of molecule  $\text{cm}^{-3}$ ):[O<sub>3</sub>]= 7×10<sup>11</sup>molecule  $\text{cm}^{-3}$ (Atkinson, 2000);  $[C1] = 5 \times 10^3$  atom cm<sup>-3</sup>, 24-h average (Pzsenny et al., 1993; Wingenter et al., 1996);  $[C1] = 1 \times 10^5$  atom cm<sup>-3</sup>, peak value observed under specific circumstances in marine regions (Spicer et al., 1998); [OH]= 10<sup>6</sup> radicals cm<sup>-3</sup>(Prinn et al., 2001).

**Table 1.**Rate coefficients for the reaction of C<sub>3</sub>F<sub>7</sub>CH=CH<sub>2</sub> with O<sub>3</sub>, Cl and OH obtained in this work

Radical	$\boldsymbol{k}$ (cm <sup>3</sup> molecule <sup>1</sup> s <sup>-1</sup> )	τ( days)
<b>O</b> 3	$(2.34\pm0.42)\times10^{-19}$	70.7
Cl	$(1.12\pm0.18)\times10^{-10}$	19.5/1.0
OH	$(1.24\pm0.18)\times10^{-12}$	9

The approximate nature of these lifetime estimated should be stressed; the average daily concentration of OH radicals and O<sub>3</sub> in the atmosphere varies significantly with both location and season (Klecka et al., 2000). The values above are estimated of global average lifetime; local lifetime could be different from those mentioned above. C<sub>3</sub>F<sub>7</sub>CH=CH<sub>2</sub> will not undergo photolysis (Orkin et al., 1997) and are not expected to be removed effectively by either wet or dry deposition (Sulbaek Andersen et al., 2005). Cl atoms are not present in the atmosphere in sufficient quantify to impact the lifetime of our compounds except in marine regions. Hence, the reaction with OH is expected to be the major loss mechanism for these fluorinated olefins. The overall atmospheric lifetime of C<sub>3</sub>F<sub>7</sub>CH=CH<sub>2</sub> is then expected to be 9 days with removal occurring approximately 90% via reaction with OH and 10 % via reaction with O<sub>3</sub>. Following its release into the environment, it is expected that C<sub>3</sub>F<sub>7</sub>CH=CH<sub>2</sub> will survive long-range transport in the atmosphere. There are three necessary conditions for C<sub>3</sub>F<sub>7</sub>CH=CH<sub>2</sub> emissions to make a significant contribution to the perfluorocarboxylic acid burden observed in remote areas. First, the emission of these compounds must reach a significant level. Second, the reaction products must survive long range transport and finally, the production yield of perfluorocarboxylic acid must be significant.

## **3.** Products of the reaction of C<sub>3</sub>F<sub>7</sub>CH=CH<sub>2</sub> with Cl and O<sub>3</sub>

In this case, GC-MS/SPME was employed as the detection technique in the 264Latmospheric simulation chamber. In the Cl reactions halogenated ketones and alcohols were detected ( $C_3F_7COCH_2Cl$  and  $C_3F_7CHOHCH_2Cl$ ), while in the in the ozone reaction, the perfluorocarboxylic acid ( $C_3F_7C(O)OH$ ) and formic acid were identified. All results suggest that the presence of the C-C double bond renders $C_3F_7CH=CH_2$ reactivity.

The initial step in the reaction with Cl is the electrophilic addition of Cl to the double bond. Addition occurs at the terminal and central carbon. To give  $C_3F_7C$ ·HCH<sub>2</sub>Cl and  $C_3F_7C$ HClC·H<sub>2</sub> radicals. Secondary radicals are generally more stable than primary radicals, therefore, from a thermodynamic perspective, it is expected that addition will occur predominately at the terminal carbon atom.
In the case of the reaction with  $O_3$  the initiation involves the concerted cycloaddition of ozone to the double bond, generating an intermediate species. Cyclo-reversion, involving homolytic cleavage of the remaining C-C and the one of the O-O bonds, gives rise to the formation of two pairs of products, in each case a carbonyl molecule and a carbonyl oxide reactive intermediate. The analysis of the products obtained in a study leads us to think that there are two reaction ways, although their respective yield could not be calculated. On the one hand, the detection of the acid, takes us to the first way, which has been detected in others studies by the formation of formaldehyde (Protczak and Treszczynzki 2002); a compound that we have not been able to detected since the CG-MS is unable to do so and when using the FTIR overlapping of bands took place. On the other hand, the second reaction way has been detected by the formation of formic acid.

# Conclusions

- The kinetic of OH depends on temperature but not on pressure.
- In the troposphere, C<sub>3</sub>F<sub>7</sub>CH=CH<sub>2</sub>is expected to mainly react with OH, and Cl in marine regions.
- The presence of the C-C double bond renders  $C_3F_7CH=CH_2$  high reactivity toward OH radicals and Cl atoms, resulting in a short tropospheric lifetime and avoiding its accumulation in the troposphere and minimizing the direct effect on the global warming of Earth.
- The product study suggests that the reaction with Cl occurs by electrophilic addition of this radical, predominately at the terminal carbon atom.
- The  $O_3$  reaction occurs by cycloaddition of the radical to the double bond, generating an intermediate species. The analysis of the products obtained in a study leads us to think that there are two reaction ways, although their respective yield could not be calculated.

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# KINETIC STUDY OF THE CI AND NO<sub>3</sub>-INITIATED PHOTO-OXIDATION OF UNSATURATED (ALLYL AND VINYL) ETHERS UNDER SIMULATED ATMOSPHERIC CONDITIONS

J. P. Aranguren Abrate<sup>a</sup>, I. Colmenar<sup>b,c</sup>, <u>S. Salgado<sup>b,c</sup></u>, E. Martínez<sup>b,c</sup>, B. Cabañas<sup>b,c</sup>, <u>P. Martín<sup>b,c</sup></u>.

<sup>a</sup> Instituto de Investigaciones en Fisicoquímica de Córdoba (INFIQC), Departamento

de Fisicoquímica, Facultad de Ciencias Químicas, Centro de Laser de Ciencias Moleculares, Universidad Nacional de Córdoba, Córdoba, Argentina

<sup>b</sup> Departamento de Química Física, Facultad de Ciencias y Tecnologías Químicas, Universidad de Castilla La Mancha. Avda Camilo José Cela S/N, 13071. Ciudad Real, Spain.

<sup>c</sup> Instituto de Combustión y Contaminación Atmosférica (ICCA), Universidad de Castilla La Mancha, Camino

Moledores S/N, 13071 Ciudad Real, Spain

Kinetic studies on the gas-phase reactions of NO<sub>3</sub> radicals and Cl atoms with 2-chloroethyl vinyl ether (2ClEVE), allyl ether (AE) and allyl ethyl ether (AEE) have been performed in a 50 L Pyrex glass reactor at (298 ±) 2 K and (700 ± 1) Torr of total pressure in synthetic air using in situ FTIR spectroscopy to monitor the reactants. Using a relative kinetic method rate coefficients (in units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) of (3.38 ± 0.34) x 10<sup>-10</sup>, (4.67 ± 0.48) x 10<sup>-10</sup> and (6.65 ± 0.65) x 10<sup>-10</sup> have been obtained for the reaction of Cl with AEE, AE and 2ClEVE, respectively, (9.21 ± 2.62) x 10<sup>-15</sup>, (1.19 ± 0.36) x 10<sup>-14</sup> and (4.85 ± 0.58) x 10<sup>-13</sup> for the reaction of NO<sub>3</sub> with AEE, AE and 2ClEVE, respectively. The reference compounds were: 1-butene and 2-metyl-propene for reactions with Cl atoms and 1-butene, propene, 2-metyl-propene and t-2-butene for reactions with NO<sub>3</sub> radicals. Atmospheric implications of the ethers unsaturated emission are briefly discussed. These are first data reported for the atmospheric reactions.

Keywords: Allyl ethers, rate coefficients, Cl atoms, NO3 radical, gas phase.

# Introduction

Oxygenated volatile organic compound (OVOCs) involved in key atmospheric processes and plays a central role in the chemical processes that determine the oxidizing capacity of the atmosphere (Singh et al., 2001; Lewis et al., 2000).

Vinyl ethers are used in different industries as solvents, motor oil additives, for the manufacturing of coatings or as intermediates for the synthesis of flavors, fragrances and pharmaceuticals (George et al., 2005). Particularly, 2-chloroethyl vinyl ether is used in manufacturing of anesthetics, sedatives and cellulose ethers (Merk Index, 2001). Allyl ethers and allyl derivatives of carbohydrates are used in the synthesis of copolymers, in coatings, inks and in the preparation of air-drying prepolymers or oligomers (Kirk et al., 2007). In the atmosphere, the primary reaction of these organic compound can occur with many atmospheric oxidant such as OH (in the day-time), NO<sub>3</sub> (in the night-time), and Cl (in the marine environment and coastal areas). The chemical degradation initiated by OH radical is a major loss pathway for atmospheric vinyl and allyl ether.

However, in marine areas and polar regions with high concentration of Cl atoms, especially during sunrise events, reactions with Cl atoms have been postulated to be an additional and significant removal process of vinyl and allyl ether. It was reported that the peak concentration of Cl atoms is as high as  $10^4$ - $10^5$  atoms cm<sup>-3</sup> in the marine boundary layer (Spicer et al., 1998).

On the other hand, since the  $NO_3$  radical is found in the night-time troposphere in concentrations higher than  $8 \times 10^7$  radicals cm<sup>3</sup> it seem that nitrate radical may dominated the chemistry of such OVOCs under dark conditions (Wayne et al., 1991).

To date, only a limited number of experiment kinetic studies have been performed on reactions of vinyl ethers with OH radical (Perry et al., 1977; Thiault et al., 2002; Thiault and Mellouki, 2006; Zhou et al., 2009; Peirone et al., 2011), NO<sub>3</sub> radicals (Zhou et al., 2009, Scarfogliero et al., 2006) and Cl atoms (Wang et al., 2009) On the other hand, as far as we know, the only result found on literature concerning allyl ether is with OH radical (Peirone et al., 2011).

In this work we report, for the first time, the rate constants for gas-phase reactions of Cl atoms and  $NO_3$  radicals with AEE, AE and 2ClEVE:

 $Cl + CH_3CH_2OCH_2CH = CH_2 \rightarrow Products$  (*k*<sub>1</sub>)

 $Cl + O(CH_2CH=CH_2)_2 \rightarrow Products$  (k<sub>2</sub>)

 $Cl + ClCH_2CH_2OCH = CH_2 \rightarrow Products$  (k<sub>3</sub>)

<sup>•</sup> To whom all correspondence should be addressed: E-mail: sagrario.salgado@uclm.es

$$NO_3 + CH_3CH_2OCH_2CH = CH_2 \rightarrow Products$$
 (k<sub>4</sub>)

 $NO_3 + O(CH_2CH=CH_2)_2 \rightarrow Products$  (k<sub>5</sub>)

$$NO_3 + ClCH_2CH_2OCH = CH_2 \rightarrow Products$$
 (*k*<sub>6</sub>)

# **Experimental section**

## Relative rate measurement

The second-order rate constants ( $k_1$ - $k_6$ ) at 298  $\pm$  2 K and a pressure of (700  $\pm$  1) Torr in N<sub>2</sub> were determinated using the relative rate method. This method relies on the assumption that both compounds in the reaction mixture, ether (S) and the reference compound (R), are removed solely by their reaction with oxidant X (where X= NO<sub>3</sub> or Cl):

$$X + S \rightarrow \text{products} \quad (k_s) \tag{1}$$

$$X + R \rightarrow \text{products} (k_R)$$
 (2)

Assuming that ether and the reference compound are only consumed by reaction with X, the kinetic treatment for the reactions expressed by Eq. (1) and (2) yields the following relationship:

$$\ln \frac{[S]_0}{[S]_t} = \frac{k_s}{k_R} \ln \frac{[R]_0}{[R]_t}$$
(3)

where  $[S]_0$ ,  $[R]_0$ ,  $[S]_t$  and  $[R]_t$  are the initial concentration and concentration at time *t* for ether and the reference compound, respectively. Two reference compounds with each oxidant were used to ensure that the reference compound does not have any influence on global rate coefficient. The reference compounds have been chosen considering that: 1) They must have a well-defined absorption band that can be monitored to follow the reaction and which does not overlap with the studied compound. 2) They must have a rate coefficient

of the same order of the studied compound so that both compounds can be perfectly followed through the reaction time.

Thus, a plot of  $\{\ln([S]_0/[S]_t)\}$  versus  $\{\ln([R]_0/[R]_t)\}$  should be a straight line that passes through the origin. The slope of this line gives the ratio of rate coefficients  $k_S/k_R$ . The absolute rate coefficient,

 $k_s$ , can therefore be obtained if the rate coefficient  $k_R$  of the reference compound is known. The reactions studied were measured relative to the reaction of different reference standards (Atkinson et al., 1982).

All experiments were performed using a 50 L Pyrex glass reaction chamber in conjunction with Fourier Transform Infrared absorption spectroscopy (FTIR) as a detection technique. The chamber was equipped with a While-type multiple-reflection mirror system (Saturn Series Multi-Pass cells) with a total optical path length of 200 m. The IR spectra were recorded with a spectral resolution of 1 cm<sup>-1</sup> using a Thermo Nicolet 5700 FT-IR spectrophotometer equipped with a KBr beam splitter and a liquid nitrogen-cooled mercury-cadmium-telluride (MCT) detector. Typically, for each spectrum, 60 interferograms were co-added over 1 min and approximately 30 spectra were recorded per experiment.

The reactants were injected into the reaction chamber using a vacuum line. A pumping system consisting of a rotary pump (Varian DS 302) was used to evacuate the reactor after every experiment. NO<sub>3</sub> radicals were produced by thermal decomposition of N<sub>2</sub>O<sub>5</sub> (Atkinson and Aschmann, 1984) in N<sub>2</sub>, which was synthesized according to the method described by Schott and Davidson (1958):

$$N_2O_5 \leftrightarrow NO_2 + NO_3$$
 (4)

For the Cl reaction, the atoms were generated by continuous photolysis of  $Cl_2$  in nitrogen. The total photolysis time was 30 min.

The initial concentration of AEE, AE, 2CIEVE and the compounds used as reference were in the range 3-9 ppm, the concentration of Cl atom precursor,  $Cl_2$ , were 10 ppm and NO<sub>3</sub> radical with typical concentration of 1-2.5 ppm.

# Reagents

2-chloroethyl vinyl ether (99%, Aldrich); allyl ether (98%, Aldrich); allyl ethyl ether (95%, Aldrich); butane (99%, Aldrich); propene (99%, Aldrich); 2methyl-propene (99%, Aldrich); *t*-2-butene (99%, Aldrich); Synthetic Air (Praxair Ultrahigh purity); N<sub>2</sub> (Praxair Ultrahigh purity); Cl<sub>2</sub> (>99.8%, Praxair).

# **Results and discussion**

The second-order rate constants were determined at  $(298 \pm 2)$  K and  $(700 \pm 1)$  Torr and obtained from the relative loss of the unsaturated ethers vs that of the reference compounds in the presence of Cl or NO<sub>3</sub>.

The reactions of NO<sub>3</sub> radicals and Cl atoms with the reference compounds used in this work are the following:

$Cl + 2$ -methyl propene $\rightarrow$ Products	$(k_7)$
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Cl + 1-butene	$\rightarrow$ Products	$(k_8)$
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$$NO_3 + 2$$
-methyl propene  $\rightarrow$  Products (k<sub>9</sub>)

 $NO_3 + t-2$ -butene  $\rightarrow$  Products  $(k_{10})$ 

 $NO_3 + 1$ -butene  $\rightarrow$  Products  $(k_{11})$ 

$$NO_3 + propene \rightarrow Products$$
 (*k*<sub>12</sub>)

where  $k_7 = (3.38 \pm 0.48) \times 10^{-10}$ ,  $k_8 = (3.0 \pm 0.4) \times 10^{-10}$ ,  $k_9 = (3.32 \pm 0.99) \times 10^{-13}$ ,  $k_{10} = (3.91 \pm 0.31) \times 10^{-13}$ ,  $k_{11} = (1.25 \pm 0.50) \times 10^{-14}$  and  $k_{12} = (9.54 \pm 3.8) \times 10^{-15}$  (Ezell et al., 2002; Orlando et al., 2003). All the *k* values are in units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

The rate constants  $k_1 - k_6$  were obtained from the ratio  $k_s/k_R$  as the value of  $k_R$  was know. The ratio of the rate constants was obtained from the slopes of the plots shown in *Figure 1*, and these were calculated from linear least-squares analysis of the experimental data using Eq. (3).



Figure 1. Example of plots of  $\{ln([AEE]_{o}/[AEE]_{i})\}$ versus  $\{ln([R]_{o}/[R]_{i})\}$  for the reaction of Cl with AEE using two different reference compounds.

The corresponding second-order rate coefficients (k in units of  $cm^3$  molecule<sup>-1</sup> s<sup>-1</sup>) are:

$$\begin{split} k_1 &= (3.38 \pm 0.34) \ge 10^{-10} \\ k_2 &= (4.67 \pm 0.48) \ge 10^{-10} \\ k_3 &= (6.65 \pm 0.65) \ge 10^{-10} \\ k_4 &= (9.21 \pm 2.62) \ge 10^{-15} \\ k_5 &= (1.19 \pm 0.36) \ge 10^{-14} \\ k_6 &= (4.85 \pm 0.58) \ge 10^{-13} \end{split}$$

The quoted values are the average of the second-order rate constant values of all the independent experiments performed for the study of each reaction. The errors quoted are twice the statistical deviation  $(2\sigma_{n-1})$  arising from the average of the values obtained in the independent experiments and do not include uncertainties from reference rate constants. An additional 15% could be considered to take into account the systematic error.

An important component of the environmental impact of an OVOCs is its global lifetime,  $\tau_{global}$ , in the atmosphere, which is the sum of the individual sink processes. It can be obtained considering the following expression:

$$\tau_{global} = \left[\frac{1}{\tau_{cl}} + \frac{1}{\tau_{oH}} + \frac{1}{\tau_{NO_3}} + \frac{1}{\tau_{O_3}} + \frac{1}{\tau_{pho.}} + \frac{1}{\tau_{other \, processes}}\right]^{-1}(5)$$

The lifetimes calculated using the relationship  $\tau_x = 1/k_x$  [X] are summarized in *Table 1*, considering average global concentrations of NO<sub>3</sub> radicals and Cl atoms of 5 x 10<sup>8</sup> radicals cm<sup>-3</sup> (Shu and Atkinson, 1995) and 1 x 10<sup>3</sup> atoms cm<sup>-3</sup> (Platt and Janssen, 1995). Unfortunately, there are no available data for reactions of 2ClEVE, AE and AEE with O<sub>3</sub> molecules. However, as it is shown in *Table 1*, the atmospheric lifetimes respect to reactions with OH radical, Cl atoms and NO<sub>3</sub> radicals range from 0.8 to 5.9 hours suggesting that these three loss processes can make significant contributions to the atmospheric degradation of the studied ethers.

*Table 1. Estimated atmospheric lifetime of the three studied ethers with OH radical NO*<sub>3</sub> *radical and Cl atoms.* 

OVOC	$ au_{OH}^{a}\left(h ight)$	$\tau_{NO3}$ (h)	$\tau_{Cl}\left(h\right)$	$\tau_{global}\left(h ight)$
AEE	6.6	60.3	822	5.9
AE	4.1	46.7	595	3.8
<b>2CIEVE</b>	3.0	1.15	418	0.8
an	•	0011		

<sup>a</sup>Peirone et al., 2011

Atmospheric photolysis is another potential loss process, but Nieto-Gligorovski et al. (2009) measured the UV absorption cross-sections of a series of vinyl ethers and they observed that the absorption vanishes above 225 nm with values of  $\sigma$  smaller than 1 x 10<sup>-21</sup> cm<sup>2</sup> molecule<sup>-1</sup>. Therefore, it is reasonable to assume that the tropospheric photolysis of the four studied ethers is negligible. The term "other processes" takes into account other loss processes in the atmosphere such as dry and wet deposition, heterogeneous reactions, etc. The studied ethers are

expected to be sparingly soluble in water -e.g., Henry's law coefficient for 2ClEVE and a series of saturated ethers is lower than 10 M atm<sup>-1</sup> at 298 K (Sander, 1999) so that wet deposition is unlikely to be of importance. Finally, the volatility of these compounds will render dry deposition an unlikely removal mechanism.

The estimated lifetimes are based on the assumption of a uniform distribution of the compounds emitted into the troposphere; however, the calculated lifetimes do not ensure such condition so that the actual lifetime of these compounds will depend on local atmospheric conditions and season. The short lifetimes show that they will be quickly degradated when emitted to the atmosphere and will be involved in tropospheric chemistry on local to regional scales.

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# Peroxy Radical Isomerisation and Hydroxyl Radical Recycling in Isoprene Oxidation: Upgraded Mechanism LIM1

Jozef Peeters<sup>\*</sup> and Son Vinh Nguyen, University of Leuven (Belgium); Jean-François Muller and Trissevgeni Stravrakou, Belgian Institute for Space Aeronomy, Brussels

\* e-mail: Jozef.Peeters@chem.kuleuven.be

The Leuven Isoprene Mechanism (proof-of-concept version LIM0, Peeters et al. 2009; Peeters and Muller 2010) explains OH regeneration in isoprene-rich, low-NO areas by novel, theoretically characterized pathways, which have all found recent experimental support: (i) interconversion of the thermally labile beta-OH- and delta-OH-isoprenylperoxy isomers; (ii) 1,6-H shift isomerisation of the Z-delta-OH-peroxys yielding hydroperoxy-enals (HPALDs); (iii) OH recycling by fast HPALD photolysis and subsequent chemistry.

The upgraded LIM1 mechanism is based on much higher levels of theory that also account for London dispersion and predict ca. 1.5 kcal/mol higher stabilities for the crucial H-bonded structures. Compared to LIMO, this results in (a) nearly the same, ~1 s<sup>-1</sup> 1,6-H shift rate of the Z-delta-OH-peroxys but substantially lower populations of these isomers; (b) slower conversion of beta-OH- to Z-delta-OH-peroxys; and hence (c) lower bulk-peroxy isomerisation rates, consistent with experiment (Crounse et al. 2011) though shown by us to depend on the peroxy lifetime. Beside HPALD formation, another major pathway following peroxy isomerisation was identified. The predicted beta  $\leftrightarrow$ delta interconversion rates and Z-delta populations are supported by the experimental temperature dependence of the HPALD yields and by their C<sub>5</sub>D<sub>8</sub>/C<sub>5</sub>H<sub>8</sub> ratio (Crounse et al., 2011). The predicted overall peroxy isomerisation yield at long peroxy lifetimes was recently confirmed within 30% by new laboratory data (Crounse et al., 2014). The subsequent chemistries for both pathways above, found to result both in OH recycling via several (newly proposed) mechanisms including photolysis, will be discussed in detail. Results of LIM1-based box modeling of the isomerisation yields as function of the peroxy lifetime, temperature and other parameters will be presented. The LIM1-based, IMAGES-modeled global distribution of the peroxy isomerisation yield with global average 30% will be discussed.

# A Computational Study of the Thermochemistry of $N_2O_5$ and the Kinetics of the Reaction $N_2O_5 + H_2O \rightarrow 2$ HNO<sub>3</sub>

Paul Marshall<sup>\*</sup> and Ionut M. Alecu University of North Texas Denton, TX 76203

# Abstract

New estimates for the thermochemistry of  $N_2O_5$  over the temperature range 0–3000 K are derived from anharmonic conformationally-averaged partition functions computed using the multi-structural method for torsional anharmonicity (MS-T). In addition, multi-structural canonical variational-transition-state theory with multidimensional tunneling (MS-CVT/MT) is employed to study the kinetics for hydrolysis of  $N_2O_5$  between 180 K and 1800 K based on stationary points computed at the CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/MG3S level of theory. The internal rotations in  $N_2O_5$  are found to generate three nearly isoenergetic torsional conformations that each make important contributions to the partition function even at low temperatures, leading to computed room temperature values for the entropy and — by virtue of a Third Law analysis — the enthalpy of formation of  $N_2O_5$ that support the recent NASA JPL recommendations while calling into question previous tabulations. The four ring-like torsional conformations located for the transition state for  $N_2O_5$  hydrolysis do not all make appreciable contributions to the partition function until higher temperatures; consequently, the cumulative effect of torsional anharmonicity in this reaction system is shown to actually decrease the thermal rate constant by nearly a factor of 3 at 298 K as opposed to increasing it by three orders of magnitude as previously proposed.

# Keywords

Dinitrogen Pentoxide, Torsional anharmonicity, Thermochemistry, Kinetics.

# Introduction

Nocturnal reaction pathways involving nitrogen oxides in the atmosphere consume ozone while also depleting the concentrations of  $NO_x$  and volatile organic compounds and thus play a critical role in counteracting the daytime generation of photochemical smog. A key reaction sequence in the nighttime removal of  $NO_x$  is the formation of dinitrogen pentoxide ( $N_2O_5$ ) and its subsequent hydrolysis:

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{R1}$$

 $NO_3 + NO_2 \rightleftharpoons N_2O_5$  (R2)

$$N_2O_5 + H_2O \rightarrow 2 \text{ HNO}_3 \tag{R3}$$

The nitrate radical  $(NO_3)$  — an important nighttime oxidant — is largely consumed by reactions with volatile organic compounds, but the less reactive dinitrogen pentoxide is thought to be lost mainly via dry deposition and heterogeneous hydrolysis to nitric acid (Crowley et al.), which represents an overall sink for nitrogen oxides in the troposphere and in the stratosphere.

Despite the important role of  $N_2O_5$  in regulating the  $NO_x$  concentration in the atmosphere, its chemistry has received relatively limited experimental attention in the

literature. In addition to challenges associated with its synthesis and thermal stability, the coupling between the two internal rotations in N<sub>2</sub>O<sub>5</sub> to each other and to the overall rotation of the molecule also makes it difficult to unambiguously resolve and assign its spectral characteristics. The structure of N<sub>2</sub>O<sub>5</sub> is also problematic in theoretical explorations as conventional theoretical interpretations of vibrational modes based on the rigid rotor harmonic oscillator (RRHO) model or even separable one-dimensional models for treating hindered internal rotations become invalid in situations which such complicated vibrational in and rovibrational coupling effects arise. As a consequence, fundamental properties critical to modeling atmospheric processes involving NO<sub>x</sub> species, such as the thermochemistry of N2O5, are not firmly established. For example, estimates for the entropy of this species — which is particularly sensitive to the two low vibrational frequencies corresponding to the coupled torsional modes - vary by as much as 9.2 J mol<sup>-1</sup> K<sup>-1</sup>. In a recent article (Alecu and Marshall, 2014), we used the comprehensive treatment of coupled torsions afforded by the multi-structural method for torsional anharmonicity (MS-T) (Zheng et al., 2011) to derive a new accurate estimate for the entropy of N<sub>2</sub>O<sub>5</sub> in order to eliminate this uncertainty in the entropy. Furthermore, we were also able obtain a more firm value for the enthalpy of formation of N<sub>2</sub>O<sub>5</sub> via a Third Law analysis using this new value for entropy computed with the more accurate model of the two coupled torsional modes and the experimental

<sup>•</sup> To whom all correspondence should be addressed

equilibrium constants for R2 measured by Osthoff et al. (2007), which we further validated via a directly computational approach involving the application of coupled cluster methods to the isodesmic reaction R3. These new thermochemical estimates for  $N_2O_5$  are discussed and compared to previous values in the next section of this article.

Another yet unresolved matter in the literature concerns the kinetics of N<sub>2</sub>O<sub>5</sub> hydrolysis (R3). Measurements made during smog chamber studies have revealed that the homogenous gas-phase hydrolysis of N<sub>2</sub>O<sub>5</sub> is a much slower process than its heterogeneous counterpart under conditions of practical interest to the atmosphere. Because of the sizable discrepancy between the rate constants for these two processes, even minute contributions from the heterogeneous reaction channel — which can readily occur at the chamber wall surface - could significantly increase the apparent overall reaction rate measured in the smog chamber experiments. Precise quantification of wall effects is challenging and often impractical, such that in most of the smog chamber investigations of R3, the observed rate constants represent upper limits to the true rate constant for the purely homogeneous process. The latest determination of  $k_3$ , 2.5 × 10<sup>-22</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, was obtained from the smog chamber experiments of Wahner et al. (1998), in which the wall effects were minimized through a significant reduction of the chamber's surface-to-volume ratio. Their determination also serves as the basis for the recommendation adopted in the most recent critical evaluation of kinetic data for atmospheric chemistry (Sander et al., 2011). However, more recently Brown et al. (2006) also showed that the atmospheric lifetime of dinitrogen pentoxide was longer than expected based on gas-phase hydrolysis alone under conditions where these particles were sparse, suggesting that  $k_3$  may have still been overestimated in the smog chamber experiments.

The hydrolysis of N<sub>2</sub>O<sub>5</sub> has also been explored theoretically using computational quantum chemistry methods. The initial density functional theory (DFT) investigations by Hanway and Tao, (1998), and second-order Møller-Plesset perturbation theory (MP2) studies by McNamara and Hillier, (2000).demonstrated that there is a significant reaction barrier to R3. In a subsequent study, Voegele et al., (2003), used canonical variational-transition-state theory with small curvature tunneling (CVT/SCT) to obtain the first theoretical estimates of the rate constant for N<sub>2</sub>O<sub>5</sub> hydrolysis. Using the more accurate G3B3 and G3(MP2)B3 composite methods, Voegele et al. confirmed that the reaction pathway identified by McNamara and Hillier involving a six-membered ring transition state was substantially (~36 kJ mol<sup>-1</sup>) lower than that for the channel proceeding through a fourmembered ring transition state originally proposed for this reaction by Hanway and Tao. Ultimately, the dynamics calculations of Voegele et al. yielded a rate constant for R3 at 298 K of  $5.2 \times 10^{-25}$  cm<sup>3</sup> molecule<sup>-1</sup>

 $s^{-1}$ , which is about a factor of 500 slower than that obtained in the smog chamber experiments of Wahner et al. This computed value for  $k_3$  included corrections for the torsional anharmonicity present in this reaction system, the overall effect of which was to significantly increase the computed rate constant by a factor of nearly 1000. The magnitude of this torsional correction is unusually large for a relatively small reaction system at 298 K. In our recent reinvestigation of this reaction system, we disputed the value of this torsional anharmonicity factor on the basis that the more comprehensive treatment of the coupled torsional motions in N<sub>2</sub>O<sub>5</sub> and the TS for R3 carried out using MS-T showed that the overall effect of the torsional anharmonicity in this reaction system is not just significantly smaller than proposed but actually leads to a reduction of  $k_3$  by about a factor of 3 at 298 K (Alecu and Marshall, 2014). This reduction was justified on the grounds that, at low and intermediate temperatures, the effects of torsional anharmonicity in  $N_2O_5$  are more pronounced than those present at the TS as a consequence of the highly constrained internal rotations in the ring-like TS and the more substantial energy difference between its torsional conformers. The thermal rate constants obtained for R3 in our article via multi-structural canonical variationaltransition-state theory with multidimensional tunneling (MS-CVT/MT) (Yu et al., 2011) are further discussed and compared to prior experimental and theoretical values in this document.

# Thermochemistry of Dinitrogen Pentoxide

The partition functions obtained via the MS-T method account for the effects of torsional anharmonicity in species with multiple torsions by properly including the Boltzmann-weighted contributions of all the structures that can be generated through the coupling of torsions and by reasonably approximating the multidimensional anharmonic potentials that connect these minima (Zheng et al., 2011). In addition, provisions are made in the MS-T treatment to account for the coupling between torsions to each other and to the overall rotation via the Kilpatrick-Pitzer scheme (Kilpatrick and Pitzer, 1949). The MSTor program (Zheng et al., 2012) used in this work computes the anharmonic partition functions using the MS-T method, and then calculates the thermochemical parameters of interest via standard relations from statistical mechanics.

Three torsional conformers were located for  $N_2O_5$  — two of these are non-superposable mirror image structures within the  $C_2$  point group while the third is a Cs structure 0.28 kJ mol<sup>-1</sup> higher in energy than the degenerate  $C_2$  structures. Based on these three structures, the MSTor program was used to evaluate the enthalpy  $H^\circ$ , constant pressure heat capacity,  $C_p^\circ$ , and entropy  $S^\circ$  for  $N_2O_5$  over the temperature range 0–3000 K at a standard state pressure of 1 bar. Including the contributions from all three torsional conformers in

the partition function via the MS-T formalism leads to computed room temperature values for the entropy and - by virtue of a Third Law analysis based on this new entropy estimate and recent measurements by Osthoff et al. (2007) of the equilibrium constants for R2 — the enthalpy of formation of N<sub>2</sub>O<sub>5</sub> that both support the latest NASA JPL recommendations (Sander et al., 2011) while calling into question the values listed in the NIST JANAF tables (Chase et al., 1985), as can be seen in Table 1. Also listed in Table 1 is the ab initio  $\Delta_{\rm f} H^{\circ}_{298.15}$  value derived from our CCSD(T)-F12a/ccpVTZ-F12//M06-2X/MG3S calculation of the reaction energy for R3 combined with thermal correction for N<sub>2</sub>O<sub>5</sub> computed from the MS-T partition function for this species and the literature values for the experimental heats of formation for H<sub>2</sub>O and HNO<sub>3</sub> and thermal corrections for N<sub>2</sub> and O<sub>2</sub>, as explained in the original article (Alecu and Marshall, 2014). This value is in good agreement with the value obtained for  $\Delta_{\rm f} H^{\circ}_{298.15}$  of N<sub>2</sub>O<sub>5</sub> via the Third Law analysis.

Table 1. Thermochemical parameters for  $N_2O_5$ 

$\Delta_{\rm f} H^{\circ}_{298.15}$ (kJ mol <sup>-1</sup> )	S° <sub>298.15</sub> (J mol <sup>-1</sup> K <sup>-1</sup> )	Reference
11.30	346.6	NIST-JANAF
$13.3\pm1.5$	$355.7 \pm 7$	NASA-JPL
$13.5\pm0.6$	353.5	Alecu and Marshall
		(ab initio)
$14.3\pm0.5$		Alecu and Marshall
		(3rd Law)

# **Kinetics of Hydrolysis Reaction**

Four torsional conformations were found for the transition state for R3, which, as shown in Figure 1, can be sub-grouped into two sets of non-superposable mirror image pairs separated by nearly 8 kJ mol<sup>-1</sup>. In contrast to  $N_2O_5$ , not all the structures for the TS make appreciable contributions to the partition function at low and intermediate temperatures due to significantly higher energy separation and highly constrained torsions in these ring-like species.



Figure 1. Torsional conformations of TS for R3

Consequently, the cumulative effect of torsional anharmonicity in this reaction system is to actually decrease the thermal rate constant at temperatures below 1800 K, as shown in Table 2, with the most significant decrease occurring over the temperature range of 180-400 K and amounting to nearly a factor of 3. This is in stark disagreement with the previously proposed three-order-of-magnitude increase in the thermal rate constant at 298 K due to torsions (Voegele et al., 2003). This strongly suggests that the separabletorsion approximations used to model torsional anharmonicity in the work of Voegele et al. may constitute inadequate treatments for torsions that are extensively coupled to each other and to external rotation as in the reaction system under present investigation. The rate constant for R3 reported by Voegele et al.,  $5.2 \times 10^{-25}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, is nearly 2000 times larger than the value of  $3.0 \times 10^{-28}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> we obtained in our study via MS-CVT/SCT (Alecu and Marshall, 2014). Ultimately, the MS-CVT/SCT calculations show that when properly accounting for the complex effect of torsional anharmonicity in this reaction system, the discrepancy between the computed and measured rate constants for R3 at room temperature is not resolved but rather widened.

Table 2. Rate constants for R3 ( $cm^3$  molecule<sup>-1</sup> s<sup>-1</sup>)

$T(\mathbf{K})$	$k^{\text{CVT/SCT}}$	$k^{\text{MS-CVT/SCT}}$	Torsional
			Factor
180	$4.75  imes 10^{-36}$	$1.49  imes 10^{-36}$	0.31
200	$5.54  imes 10^{-34}$	$1.72 \times 10^{-34}$	0.31
250	$3.26  imes 10^{-30}$	$1.00  imes 10^{-30}$	0.31
298.15	$9.61  imes 10^{-28}$	$3.02 \times 10^{-28}$	0.31
300	$1.15  imes 10^{-27}$	$3.62 \times 10^{-28}$	0.31
400	$2.01  imes 10^{-24}$	$6.90  imes 10^{-25}$	0.34
600	$4.45  imes 10^{-21}$	$1.89 \times 10^{-21}$	0.42
800	$2.52  imes 10^{-19}$	$1.30  imes 10^{-19}$	0.52
1000	$3.20  imes 10^{-18}$	$1.97 imes10^{-18}$	0.62
1200	$1.90 imes10^{-17}$	$1.37  imes 10^{-17}$	0.72
1500	$1.26  imes 10^{-16}$	$1.11  imes 10^{-16}$	0.88
1800	$4.91\times10^{16}$	$5.16 imes10^{-16}$	1.05

# Conclusions

New estimates for the thermochemistry of  $N_2O_5$  and the thermal rate constants for its hydrolysis reaction were derived using multi-structural partition functions that properly account for the anharmonic effects brought about by the torsions in these reaction systems. Our computational investigation (Alecu and Marshall, 2014) revealed that 3 conformers are generated by the two coupled torsions in  $N_2O_5$ , and that by accounting for the coupling between these torsions as well as their coupling to external rotation, the MS-T torsional model employed to calculate anharmonic partition functions in this work led to the derivation of accurate thermochemistry for this species. In particular, the  $S^{\circ}_{298.15}$  value for  $N_2O_5$  computed in this study using

MS-T partition functions is in very good agreement with and further supports the latest recommendations of NASA-JPL (Sander et al., 2011) over that listed at JANAF (Chase et al., 1985). A subsequent third law analysis based on this computed entropy value and the equilibrium constant measurements of Osthoff et al. (2007) for R2 led to the derivation of an experimentally-based value for which is also in agreement with the NASA-JPL recommendations. Finally, the computed thermal rate constant for the hydrolysis of N2O5 at 298.15 K computed via MS-CVT/SCT was found to be nearly a factor of 2000 smaller than that previously reported by Voegele et al. (2003), and this disagreement was shown to stem from the two different torsional models employed in these two studies. Based on our MS-T calculations, which mark the most extensive treatment of the coupled torsions in this reaction system to date, we conclude that the torsional anharmonicity in this system cannot account for the 6-order-of-magnitude discrepancy between the computed and measured rate constant for the hydrolysis of N<sub>2</sub>O<sub>5</sub> at 298.15 K. The extremely small rate constant computed for hydrolysis is in line with the suggestion by Brown et al. (2006) that the laboratory value for  $k_3$  may be too high.

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# TROPOSPHERIC DEGRADATION OF E,E-2,4-HEXADIENAL DURING THE DAY

Colmenar I.<sup>a,b</sup>, <u>Salgado S</u><sup>\* a,b</sup>, Martínez E<sup>a,b</sup>, Cabañas B<sup>a,b</sup> and <u>Martín P</u><sup>a,b\*</sup>

 <sup>a</sup> Departamento de Química Física, Facultad de Ciencias y Tecnologías Químicas, Universidad de Castilla La Mancha, Avda. Camilo José Cela S/N, 13071 Ciudad Real, Spain.
 <sup>b</sup> Instituto de Combustión y Contaminación Atmosférica (ICCA), Universidad de Castilla La Mancha, Camino Moledores S/N, 13071 Ciudad Real, Spain

# Abstract

A set of experiments have been done in order to study the mechanism and products generated in the degradation of E,E-2,4-hexadienal with OH radicals and chlorine atoms. Two experimental systems were used, a 50 L Pyrex glass reaction chamber in conjunction with Fourier Transform Infrared absorption spectroscopy (FTIR). E-butenedial, HCHO, CO and NO<sub>2</sub> are the major products of the OH-initiated oxidation of E,E-2,4-Hexadienal. Formation of formaldehyde, carbon monoxide and dioxide and NO<sub>2</sub> may be attributed to the degradation of the precursor mixture employed (CH<sub>3</sub>ONO/NO). The yield obtained for E-butenedial has been estimated in 76±2%. A double bond addition of the oxidant in C4 position has been proposed as the main tropospheric pathway for its degradation during daytime. Addition of the OH radical in C4 and subsequent reaction with oxygen and NO can explain the formation of the E-butenedial. For chlorine atoms, HCl, CO, CO<sub>2</sub>, HCOOH and a chlorinated compound were the identified products. An analogous pathway with chlorine atoms is expected to happen. Bands observed at 738, 1726 and 1745 cm<sup>-1</sup> may be attributed to the stretching mode of (C-Cl) and (C=O) of the aldehyde and chloride group respectively. The presence of these bands has been tentatively assigned to the formation of 4-oxobut-2-enoyl-chloride.

# Keywords

E,E-2,4-hexadienal, atmospheric oxidants, gas phase reaction, reaction mechanism.

# Introduction

E,E-2,4-hexadienal is an  $\alpha$ , $\beta$ -unsaturated carbonyl compound (H3CCH=CHCH=CHCHO) which can be present in the atmosphere due to the reactions of aromatic compounds such as toluene with the main tropospheric oxidants (Dumdei et al., 1988).

E,E-2,4-hexadienal due to its double bonds and aldehydic group may react with the tropospheric oxidants by double bond addition or by hydrogen abstraction. Kinetics studies developed by Colmenar et al. (2014) with chlorine atoms, OH and nitrate radicals suggested a double bond addition as the main pathway for these reactions.

The main degradation routes for this compound in the atmosphere are the reactions with OH radicals and sunlight. Besides, reactions with nitrate radical during nighttime play a determinant role (Colmenar et al., 2014).

It is known that E,E-2,4-hexadienal is photolyzed under sunlight (O'Connor et al., 2006; Colmenar et al., 2014). This process leads to a photoisomerization to a ketene-type structure, probably Ehexa-1,3-dien-1-one (O'Connor et al., 2006). Besides it is known that this compound, as high-weight carbonyl compound, easily forms aerosols. His heterogeneous reactivity with  $H_2SO_4$  has been previously studied (Zhao et al., 2005; Wang et al., 2010, 2011). To date, no products study for the homogeneous degradation of E,E-2,4-hexadienal have been published.

For this purpose a set of experiments have been done in order to study the mechanism and products generated in the degradation of E,E-2,4hexadienal with OH radicals and chlorine atoms.

# Experimental

The experimental set-up consisted into a 50 L Pyrex glass reaction chamber in conjunction with Fourier Transform Infrared absorption spectroscopy (FTIR) as a detection technique. The chamber was equipped with a White-type multiple-reflection mirror system (Saturn Series Multi-Pass cells) with a total optical path length of 200 m. The IR spectra were recorded with a spectral resolution of 1 cm<sup>-1</sup> using a Thermo Nicolet 5700 FT-IR spectrophotometer equipped with a KBr beam splitter and a liquid nitrogen-cooled mercuryecadmiumetelluride (MCT) detector. Typically, for each spectrum, 60 interferograms were co-added over 1 minute. Experiments were performed at room temperature ~  $(298\pm 2 \text{ K})$  and atmospheric pressure ~  $(700\pm 1)$  Torr in synthetic air.

OH radicals were generated by continuous photolysis of CH<sub>3</sub>ONO in the presence of NO in air at a wavelength of 360 nm using 8 actinic lamps ( $\lambda_{max}$ =

360 nm). Methyl nitrite was synthesized in our lab as has been described elsewhere (Taylor et al., 1980). Chlorine atoms were generated by VIS photolysis of  $Cl_2$  employing 8 actinic lamps ( $\lambda_{max}$ = 360 nm).

Chemicals used were as follow: E,E-2,4hexadienal (95%, Aldrich), Synthetic Air (Praxair Ultrahigh purity), Cl<sub>2</sub> (>99.8%, Praxair), NO (Praxair, 99%), CO (99.998%, Praxair), chlorhydric acid (37%, Fluka).

# **Results and Discussion**

# Degradation under visible light

Previous to the study of the degradation of E, E-2,4-hexadienal with OH radicals and chlorine atoms, its degradation under visible light was studied by FTIR. For this experiment a typical concentration around 15 ppm (parts per million) was introduced in the reaction chamber in synthetic air and the substrate was exposed to the irradiation of 8 visible or actinic lamps ( $\lambda_{max}$ = 360 nm) during 70 minutes. After this time, a consumption of the substrate > 80% was obtained. However, only bands due to the formation of CO, CO<sub>2</sub> and HCOOH were observed. These products may also have a contribution from walls reaction. No evidence of the formation of the ketene-type structure suggested by O'Connor et al. (2006) was found.

# Products with OH radicals

For the OH reactions, concentrations of 11-12 ppm for E, E-2,4-hexadienal and 15 ppm for CH<sub>3</sub>ONO and NO were used. Experiments were monitored by FTIR during 50-60 minutes. Products identification was made by comparison with NIST and our IR library.

After 55 minutes of reaction and a substrate consumption of 80%, the main detected products were E-butenedial, HCHO, CO,  $CO_2$  and  $NO_2$ . (See Figure 1) Formation of formaldehyde, carbon monoxide and dioxide and  $NO_2$  may be attributed to the degradation of the precursor mixture employed (CH<sub>3</sub>ONO/NO).



Figure 1. FTIR spectra: E, E-2,4-hexadienal (A);OH products (B); E-butenedial (C); Cl products (D).

<sup>• \*</sup>To whom all correspondence should be addressed: mariapilar.martin@uclm.es

Calibrated spectra were employed to quantify the substrate and the reaction products. Concentration of E-butenedial has been estimated based on a value of  $5.35 \times 10^{-4}$  ppm V<sup>-1</sup> m<sup>-1</sup> for the IR absorption coefficient for its isomer Z-butenedial at 1713 cm<sup>-1</sup> (Bierbach et al., 1997)

The time-concentration profiles obtained seem to be of primary products, with a progressive increase in the concentration from the first stages of the reaction. Only for CO and  $CO_2$  the obtained profiles seem to be typically for secondary products (see Figure 2).



Figure 2. Time-concentration profile of the products identified in the reaction of E, E-2,4-hexadienal with OH radicals.

Product yields were obtained from the slope of plots of the amount of product formed versus the amount of E,E-2,4-hexadienal consumed. The obtained yields were as follows:  $(76.0\pm2.0)$  %,  $(8.0\pm0.4)$  %,  $(8.6\pm0.7)$  % and  $(14.6\pm0.5)$  % for E-butenedial, CO, CO<sub>2</sub> and HCHO, respectively. High levels of NO<sub>2</sub> were monitored through the whole reaction and an estimated yield > 100% was obtained, suggesting an extra contribution due to the degradation of the (CH<sub>3</sub>ONO/NO) mixture as mentioned before.

Formation of E-butenedial may be explained by a double bond addition of the oxidant in C4 position, followed by its oxidation with oxygen and reaction with NO. Proposed mechanism is shown in Figure 3.



Figure 3. Mechanism proposed for the OH-initated oxidation of E E-2,4-hexadienal.

In these experiments chlorine atoms were generated by continuous photolysis of  $Cl_2$  with visible lamps. Typicall concentrations of 12-13 ppm for E, E-2,4-hexadienal and 15 ppm of  $Cl_2$  were employed. Experiments were performed in synthetic air as bath gas.

After 12 minutes of reaction and a consumption of E, E-2,4-hexadienal > 95%, the main detected products were chlorhydric acid, CO, formic acid and CO<sub>2</sub>. These products may be generated as a result of the interactions of the precursor and light employed with the walls chamber. Besides, CO<sub>2</sub> may also be generated in the reaction of E, E-2,4-hexadienal with chlorine atoms, as in the case of OH radicals, in the last steps of the reaction from degradation of acetaldehyde.

Obtained yields were as follow:  $(7.6\pm0.4)$  %,  $(7.4\pm0.5)$  % and  $(4.3\pm0.2)$  % for CO, CO<sub>2</sub> and HCOOH, respectively. Same primary products profile was obtained as in the case of OH reaction (see Figure 4).



Figure 4. Time-concentration profile of the products identified in the reaction of E, E-2,4-hexadienal with chlorine atoms.

Moreover, a set of bands at 1745, 1724 and 738 cm<sup>-1</sup> were observed in the product spectrum. These IR frequencies may be attributed to the stretching of (C-Cl) and (C=O) of a chloride aldehyde (see Figure 1D). These bands have been tentatively assigned to the formation of 4-oxobut-2-enoyl-chloride in the reaction with Cl atoms. However the confirmation of this product was not possible since it is not commercially available.

An analogous pathway reaction with chlorine atoms is expected to happen than in the case of OH reactions. Therefore a double bond addition in C4 position has been proposed as the main reaction channel, followed by the addition of oxygen and the reaction with peroxy radicals (RO<sub>2</sub>) (see Figure 5).

Products with Chlorine Atoms



*Figure 5. Mechanism proposed for the Cl-initated oxidation of E, E-2,4-hexadienal.* 

# Conclusions

The tropospheric reactivity of E, E-2,4hexadienal during day time have been investigated. According to the results obtained in this study, a double bond addition in C4 has been proposed as the main degradation mechanism for the reactions with OH and chlorine atoms. E-butenedial and carbon dioxide have been identified as the main degradation product of E,E-2,4-hexadienal with OH radicals. In the case of chlorine atoms, CO, CO<sub>2</sub> and 4-oxobut-2-enoylchloride were the main products detected. However this latter was not confirmed since it is not commercially available.

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# **OH Reactivity Studies of VOC Oxidation in the HIRAC Chamber**

C. A. Brumby<sup>\*1</sup>, D. R. Cryer<sup>1</sup>, L. K. Whalley<sup>1, 2</sup>, D. E. Heard<sup>1, 2</sup> and P. W. Seakins<sup>1, 2</sup> <sup>1</sup>School of Chemistry, University of Leeds, Leeds, UK <sup>2</sup>National Centre for Atmospheric Science, University of Leeds, Leeds, UK Corresponding author: cmcab@leeds.ac.uk

# Keywords

HIRAC, OH reactivity, VOCs, biofuels.

The hydroxyl radical, OH, is a key reactive species in our troposphere. It is very reactive, leading to its short lifetime of between about 0.001 and 1 second. Measurements of OH reactivity are important for our understanding of photochemical reaction mechanisms in the troposphere. OH reactivity instruments are mainly employed for field measurements and few previous studies have been reported on measurements from atmospheric chambers<sup>1-3</sup>.

$$k'_{OH} \sum_{i} k_{OH,i}[i] = \tau_{OH}^{-1}$$

The use of chambers in the study of atmospheric chemistry forms an important link between field studies and small scale laboratory based research. The HIRAC chamber is coupled to a number of analytical instruments, including a FAGE instrument for the measurement of OH and  $HO_2$  radicals<sup>4</sup>. A laser flash photolysis OH reactivity instrument has recently been coupled to the HIRAC chamber. OH reactivity measurements with the HIRAC chamber can be used as a test bed for the instrument as well as probing chemical mechanisms in a very controlled environment.

The ability to measure a wide range of VOCs in HIRAC experiments allows for comparison between measured and calculated total OH reactivity for a range of applications. Results from oxidation studies of VOCs in HIRAC will be presented, with a focus on OH initiated oxidation of alcohols (as potential biofuels) in order to determine the change in OH reactivity with time from the oxidation products. Preliminary results (Figure 2) show the change in OH reactivity following the OH initiated oxidation of *n*-butanol in HIRAC.



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# Kinetics of the unimolecular reaction of CH<sub>2</sub>OO and its reaction with the water monomer, acetaldehyde and acetone at atmospheric conditions

Torsten Berndt,<sup>*a*</sup> Ralf Kaethner,<sup>*a*</sup> Jens Voigtländer,<sup>*a*</sup> Frank Stratmann,<sup>*a*</sup> Patrick Reichle,<sup>*b*</sup> Mark Pfeifle,<sup>*b*</sup> Matthias Olzmann,<sup>*b*</sup> Mikko Sipilä,<sup>*c*</sup> Markku Kulmala<sup>*c*</sup> and Hartmut Herrmann<sup>*a*</sup>

- <sup>b</sup> Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany
- <sup>c</sup> Department of Physics, University of Helsinki, Helsinki, Finland.

Stabilized Criegee Intermediates (sCI) have been identified as oxidants of atmospheric trace gases such as SO<sub>2</sub>, NO<sub>2</sub>, carboxylic acids or carbonyls. The atmospheric sCI concentrations, and accordingly their importance for trace gas oxidation, are controlled by the rate of the most important loss processes, very likely the unimolecular reaction and the reaction with water vapour ubiquitously present in high concentrations.

In this study, the rate coefficients of the unimolecular reaction of the simplest sCI, formaldehyde oxide CH<sub>2</sub>OO, and the bimolecular reaction with the water monomer have been measured at 295 ± 2 K and atmospheric pressure using a free jet flow system. CH<sub>2</sub>OO was produced from the reaction of ozone with C<sub>2</sub>H<sub>4</sub> and CH<sub>2</sub>OO concentrations were probed indirectly detecting H<sub>2</sub>SO<sub>4</sub> after titration with SO<sub>2</sub>. The rate coefficient of the unimolecular reaction  $k_{(uni)}$  was determined from time resolved experiments supported by additional measurements performed under CH<sub>2</sub>OO steady-state conditions. Experimental results for  $k_{(uni)}$  are analyzed in terms of statistical rate theory on the basis of molecular data from quantum chemical calculations. Furthermore, the rate coefficient  $k_{(CH_2OO+H_2O)}$  has been determined for sufficient low H<sub>2</sub>O concentrations (< 10<sup>15</sup> molecule cm<sup>-3</sup>) allowing separation from the CH<sub>2</sub>OO reaction with the water dimer. In order to evaluate the accuracy of the experimental approach, the rate coefficient of the reaction of CH<sub>2</sub>OO with acetaldehyde and acetone were reinvestigated.

<sup>&</sup>lt;sup>a</sup> Leibniz-Institute for Tropospheric Research, TROPOS, Leipzig, Germany.

# Autoxidation of cyclohexenes in the gas-phase

Matti P. Rissanen<sup>\*a</sup>, Theo Kurtén<sup>b</sup>, Roy L. Mauldin III<sup>a, c</sup>, Olga Garmash<sup>a</sup>, Noora Hyttinen<sup>b</sup>, Henrik G. Kjaergaard<sup>d</sup> and Mikael Ehn<sup>a</sup>

<sup>a</sup> Department of Physics, University of Helsinki, P.O. BOX 64, FI-00014, Finland
 <sup>b</sup> Department of Chemistry, University of Helsinki, P.O. BOX 55, FI-00014, Finland
 <sup>c</sup> University of Colorado at Boulder, Boulder, CO, USA
 <sup>d</sup> Department of Chemistry, University of Copenhagen, Universitetsparken 5, 2100 Copenhagen Ø, Denmark

Keywords

Autoxidation, peroxy radical isomerization, highly-oxidized compounds, nitrate chemical ionization

Detailed knowledge of gas-phase organic oxidation reaction mechanisms is crucial for understanding and optimizing many processes of scientific and socio-economic importance. For example, energy production efficiency of combustion practices and closely related air quality issues ultimately depend on our understanding and ability to steer and influence the outcome of a chemical reaction system. Oxidation routes leading to molecular growth and subsequent decrease in volatility, by sequential oxygen addition + peroxy radical isomerization steps (i.e. autocatalytic oxidation = autoxidation<sup>1</sup>), especially important for secondary organic aerosol (SOA) production, have recently received a considerable attention due to being a potential missing piece linking the observed and theoretically predicted SOA formation yields<sup>2,3</sup>.

A suite of selected, unsaturated volatile organic compound ozonolysis reactions have been studied in atmospheric pressure flow tube experiments in order to shed light on the mechanisms producing highly-oxygenated compounds upon autoxidation in the gas-phase. The studies were performed using nitrate chemical ionization mass spectrometers (CIMS) for detection of the most oxidized species, and a suite of other ancillary measurements to monitor the gas-mixture. The laboratory experiments have been further supplemented by detailed quantum chemical computations. In the presentation, I will concentrate on a few selected cyclohexenes and their ozonolysis product spectra recorded by two different (NO<sub>3</sub><sup>-</sup>) CIMS instruments: a quadrupole and a time-of-flight instrument. The cyclohexenes were chosen as surrogates for the more abundant biogenic monoterpenes.

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# REDUCTION MECHANISEM OF TELLURIUM SPECIES FROM COPPER ELECTRO WINNING SOLUTIONS

Mohammad Mokmeli<sup>\*</sup>, David B. Dreisinger and Berend Wassink University of British Columbia – Vancouver British Columbia, V6T 1Z4

### Abstract

The presence of tellurium in copper-nickel sulphide ores results in down-stream contamination of leach solutions and electrolytes. Tellurium must be removed from leach solutions before electrowinning to prevent contamination of copper cathodes. Cuprous ion is industrially used as a reductant to remove tellurium ions. However, tellurium ions reduction kinetics with cuprous is not well-known. In this study, the slow  $Te^{VI}$  reduction steps with cuprous was identified and a plausible  $Te^{VI}$  reduction mechanism was suggested. The rate determining step was investigated by studying the kinetics of the coupled reaction of  $Te^{IV}$  and  $Te^{IV}$  with cuprous. The rate law suggested for the reduction of  $Te^{IV}$  with cuprous and the coupled kinetics equation for consecutive reduction reactions of  $Te^{IV}$  and  $Te^{VI}$  and  $Te^{VI}$  were derived. It was shown that the rate constant of the coupled reaction is very close to the rate constant calculated based on the assumption that  $Te^{VI}$  reduction is a rate-determining step.

# Keywords

Tellurium, Cuprous, Reduction mechanism, Coupled reaction, Rate determining step.

# Introduction

Tellurium and selenium must be removed from the leach solution before electrowinning to prevent contamination of the copper cathode. Contamination of copper by tellurium and selenium adversely affect the physical properties of electroplated copper. Tellurium, for example, has an adverse effect on the annealability of copper metal (Cooper, 1985).

Cuprous ion is used as a reducing agent to remove impurities in higher oxidation states such as selenium and tellurium ions from copper sulphatesulfuric acid solutions (Mokmeli et al., 2013). In addition to cuprous ion, metals with reduction potentials below those of  $Te^{VI/IV}$  or  $Te^{IV/0}$  couples may also have the thermodynamic possibility of reducing Te<sup>VI</sup> or Te<sup>IV</sup> to Te or H<sub>2</sub>Te. The stability region of tellurium species as a function of solution potential are shown in Figure 1. According to the graph, the Fe<sup>2+</sup>/Fe<sup>3+</sup> couple can only reduce Te<sup>VI</sup> to Te<sup>IV</sup>. However, the couples Cu/Cu<sup>2+</sup>, Cu<sup>+</sup>/Cu<sup>2+</sup>, Ni/Ni<sup>2+</sup> and SO<sub>2</sub>/HSO<sub>4</sub><sup>-</sup> have the thermodynamic ability to reduce Te<sup>VI</sup>/Te<sup>IV</sup> to elemental tellurium. Base metal couples of Fe/Fe<sup>2+</sup> and Zn/Zn<sup>2+</sup> can further reduce tellurium to telluride. Nevertheless, in cupric-bearing solutions, couples with electrochemical potentials below that of the cupric-copper couple will precipitate the copper as well. It is also expected that the homogeneous reduction of tellurium species with cuprous ion proceed much faster than the heterogeneous reduction of tellurium species with copper metal.



Figure 1. Thermodynamics of tellurium species reduction by different reductants at pH = 0,  $[Te] = 3 \times 10^{-4} M$ , 25°C, P SO<sub>2</sub> = 1 atm, total sulphate = 1 M.

In general, The advantages of using cuprous for removal of tellurium are that it is an environmentally clean process and it adds no impurities to copper EW electrolytes; the only soluble reactant and final product is cupric ion. (Stewart et al., 1985). The disadvantages of using cuprous are the slow reaction kinetics for reduction of Te<sup>VI</sup> with cuprous, the high air sensitivity of cuprous and the low saturated concentrations of cuprous in solution (Mokmeli et al., 2012). Tellurium removal from copper sulfate-sulfuric acid electrolyte has been practiced since 1976 at the ED (Electrowinning Department) plant of Vale-Canada by contact with cuprous ion in a fixed bed reactor followed by a solution ageing step (Stewart et al.,

Mohammad Mokmeli email address: <u>mokmeli@alumni.ubc.ca</u>

1985). High pressure oxidative leaching of a copper sulfide residue at the Vale facility dissolves the tellurium content of the residue in the form of  $Te^{IV/VI}$  species into the electrolyte. The  $Te^{IV/VI}$  species are reduced with  $Cu^+$  to form insoluble copper tellurides. An environmentally clean process and minimal introduction of impurities into process streams are the main advantages of this process. On the other hand, a long reaction time is the main drawback of the process (23 hours for a typical processing rate of 150 L/min). Therefore, the objective of this research is to provide a better understanding of the tellurium ions reduction reaction kinetics with cuprous. This can lead to a more efficient process (Mokmeli et al., 2015).

# **Materials**

All chemicals used for preparation of cuprouscontaining solutions were reagent grade or better: Na<sub>2</sub>Te(OH)<sub>4</sub>O<sub>2</sub>.xH<sub>2</sub>O and Na<sub>2</sub>TeO<sub>3</sub> (Alfa Aesar), CuSO<sub>4</sub>.5H<sub>2</sub>O A.C.S. (Fisher), copper wire, 99.9% (Alfa Aesar), H<sub>2</sub>SO<sub>4</sub>, (Fisher). Chemicals used for analysis of cuprous were analytical grade: Cerium(IV) sulfate, (Alfa-Aesar) and ferroin solution, (Fisher) or reagent grade: NH<sub>4</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O, (Sigma-Aldrich). All solutions were prepared with high purity water (18  $M\Omega$  cm) using a Nano Pure Diamond water purification system. Ultra high-purity argon (99.999% Ar) was used to purge the reactor and protect cuprous solutions from oxygen. The concentration of the cerium solution was verified by titration with analytical grade As<sub>2</sub>O<sub>3</sub>, 99.96% (Sigma-Aldrich), and using OsO<sub>4</sub> solution, 2% (Alfa Aesar).

# **Experimental Procedure**

Cuprous ion was generated in a sealed 2 L five-neck, flat bottom flask. A schematic illustration of the experimental apparatus is shown in Figure 2. The reaction vessel was immersed in a thermostatted water bath. The temperature was maintained to within  $\pm 0.3^{\circ}$ C. A slow flow of argon was maintained across the top of the apparatus. A magnetic stirrer was used to agitate the solution. Cuprous was formed by contact of the solution with a coil of copper wire at the desired temperature. Sampling from the solution was accomplished by applying positive pressure of argon gas to the reactor and forcing solution to flow through a polypropylene filter (30 µm) into a graduated cylinder containing a known mass of ~0.04 M (NH<sub>4</sub>)Fe(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O solution. This converted Cu<sup>+</sup> into the more stable  $Fe^{2+}$ , facilitating subsequent titration analysis (Fe<sup>3+</sup> + Cu<sup>+</sup> = Fe<sup>2+</sup> + Cu<sup>2+</sup>). Ferrous ion was determined by titration with cerium(IV) using an automatic burette with a resolution of 0.1  $\mu$ L (Fe<sup>2+</sup>+  $Ce^{4+} = Ce^{3+} + Fe^{3+}$ ). The endpoint was indicated by ferroin. The uncertainty in the cuprous determination was estimated to be  $\pm 0.6\%$  relative standard deviation. Potentiometry was used to follow the potential of a solution relative to a reference electrode.

Typical kinetics experiments first involved placing a copper wire coil into solution. Cuprous ion was generated by the reaction of copper wire with cupric sulfate in the acidic solution. After generation of sufficient amounts of cuprous the copper coil was taken out and the initial concentration of cuprous was analysed by titration. The reaction was initiated by adding sodium tellurate/sodium tellurite to the solution once the solution temperature stabilized at the desired value. During an experiment a series of samples were removed for analysis. The samples were filtered and after cuprous analysis the samples were sent to Vale's laboratory for total tellurium analysis by ICP-MS.



Figure 2. Schematic illustration of the apparatus.

## **Results and Discussion**

# Stoichiometry of Te<sup>IV</sup> and Te<sup>VI</sup> Reduction with Cu<sup>+</sup>

The stoichiometry of  $Te^{VI}$  and  $Te^{IV}$  reaction with  $Cu^+$  was determined by measuring the concentration changes of the cuprous to the concentration changes of tellurate/tellurite at T =95.1°C. Results are depicted in Figure 3.



Figure 3. Stoichiometry of the reduction of  $Te^{IV}/Te^{VI}$ with cuprous at  $T = 95.1^{\circ}C$  and  $[H_2SO_4] = 50 \text{ g/L}$ .

An average of  $\frac{\Delta[Cu^+]}{\Delta[Te^{VT}]}$  and  $\frac{\Delta[Cu^+]}{\Delta[Te^{TV}]}$  ratio during

the full reaction time (6 hrs for  $Te^{VI}$  and 1 hr for  $Te^{IV}$ ) were calculated as 10.05 and 8.05 for  $Te^{VI}$  and  $Te^{IV}$ reduction reactions, respectively. According to this, then stoichiometry of the overall reaction may be written as following at  $T = 95.1^{\circ}C$ :

 $H_{6}TeO_{6} + 6H^{+} + 10Cu^{+} = Cu_{2}Te + 6H_{2}O + 8Cu^{2+}$ (1)

 $TeO(OH)^{+} + 3H^{+} + 8Cu^{+} = Cu_2Te + 2H_2O + 6Cu^{2+}$ (2)

The slow step of the reduction of  $Te^{VI}$  and  $Te^{IV}$  with cuprous was identified by monitoring the cuprous concentration with time at different acidities. It was observed that for any given acid level,  $Te^{IV}$  reduces about 3-4 times faster than  $Te^{VI}$  (Mokmeli et al., 2014). However,  $Te^{IV}$  reduction was not fast enough compared to  $Te^{VI}$  to say that  $Te^{VI}$  reduction is definitely rate-determining. This means that the two reduction reactions are coupled and some build-up of  $Te^{IV}$  concentration is expected especially at the beginning of the reduction reaction. The significance of this effect has been investigated in following by studying the kinetics of the  $Te^{IV}$  reduction with Cu<sup>+</sup> and with studying the coupled kinetics equation for consecutive reduction reactions of  $Te^{IV}$  and  $Te^{VI}$ .

# Reaction Order of Te<sup>IV</sup> Reduction with Cu<sup>+</sup>

A plot of  $\ln[Cu^+]$  and  $\ln[Te^{IV}]$  over time was shown in Figure 4 over a three half-life change in cuprous and tellurium concentration and in the pseudofirst order kinetics condition. The reaction order very nearly conforms to a first order rate equation with respect to cuprous and tellurium concentration at  $[H_2SO_4] = 50$  at 95.1 °C. Hence, the reduction reaction may be written as follows:



Figure 4. Cuprous and tellurium reaction order in reduction of  $Te^{IV}$  with  $Cu^+$  at 95.1 °C and  $Cu^{2+} = 50$ g/L,  $[H_2SO_4] = 50$  g/L.

Therefore, the integrated form of the rate law is given by:

$$\ln \frac{C + [Cu^+]}{[Cu^+]} = k_2 C t + \ln \frac{10[Te^{IV}]_0}{[Cu^+]_0}$$
(4)

The rate constant (k<sub>2</sub>) was calculated by plotting  $\ln \frac{C + [Cu^+]}{[Cu^+]}$  versus time and then calculating the slope

of the best-fit straight line to the data using least squares method as 0.0328  $M^{-1}s^{-1}$  at T = 95.1°C. Similarly, the reaction order of Te<sup>VI</sup> reduction with cuprous was observed to conform to a first order rate equation with respect to both cuprous and tellurium concentration at different acidities and temperatures.

$$-\frac{d[Te^{VI}]}{dt} = k_1 [Cu^+][Te^{VI}]$$
(5)

An average rate constant for reduction of  $Te^{VI}$  at sulphuric acid concentration of 50 g/L was calculated as 0.00771 M<sup>-1</sup>s<sup>-1</sup>. Therefore, the removal rate of Te<sup>IV</sup> is 4.2 times faster than the removal rate of Te<sup>VI</sup> at similar initial tellurium and cuprous concentrations.

# Coupled Reduction of $Te^{VI}$ and $Te^{IV}$ with $Cu^{\scriptscriptstyle +}$

Kinetics scheme of consecutive irreversible reductions of  $Te^{VI}$  and  $Te^{IV}$  with cuprous can be proposed as follows:

$$\begin{cases} Te^{VI} + Cu^+ \stackrel{k_1}{\longrightarrow} Te^{IV} \\ Te^{IV} + Cu^+ \stackrel{k_2}{\longrightarrow} Cu_2 Te^{IV} \end{cases}$$

Pseudo-first order kinetics condition at almost constant cuprous concentration simplifies the  $Te^{VI}$  and  $Te^{IV}$  reduction rate laws applying Eq. (3) and 5 as follows:

$$\frac{d[Te^{VI}]}{dt} = -k_1[Te^{VI}][Cu^+] \text{ at } [Cu^+] \approx [Cu^+]_{_{0ave}} \approx \text{Constant}$$

Therefore, the Te<sup>VI</sup> concentration with time is given by:

$$[Te^{VI}] = [Te^{VI}]_0 \times e^{-k_1 t [Cu^+]_{0ave}}$$
(6)

According to the kinetics scheme, the differential rate equation for reduction of  $Te^{IV}$  is written as:

$$\frac{d[Te^{V}]}{dt} = k_1[Te^{VI}][Cu^+] - k_2[Te^{VI}][Cu^+] = k_1[Te^{VI}]_0 \times e^{-k_1 t [Cu^+]_{0_{ave}}} [Cu^+] - k_2[Te^{VI}][Cu^+]_{0_{ave}}$$

The dependence of the  $Te^{IV}$  on time can be obtained then by applying the integrating factor method, the  $Te^{VI}$  concentration with time is given by:

$$[Te^{IV}] = \frac{k_1 [Te^{VI}]_0}{k_2 - k_1} (e^{-k_1 t [Cu^+]_{0ave}} - e^{-k_2 t [Cu^+]_{0ave}})$$
(7)

Accordingly, the total tellurium concentration is

written as: 
$$[Te^{IV}] + [Te^{VI}] = [Te^{VI}]_0 \times A$$
  
Where  $A = e^{-k_1 t [Cu^+]_{0are}} + \frac{k_1 (e^{-k_1 t [Cu^+]_{0are}} - e^{-k_2 t [Cu^+]_{0are}})}{k_2 - k_1}$ 

 $Cu_2Te$  concentration is then obtained by the mass balance relationship:

$$[Cu_2Te] = [Te^{VI}]_0 - [Te^{VI}]_0 \times A$$
(8)

Reduction reaction of  $Te^{VI}$  with  $Cu^+$  at initial cuprous and tellurium concentrations of 0.0172 M and 0.000135 M, was chosen to investigate the effect of the coupled reaction. In this test cuprous concentration was kept nearly constant while tellurium concentration reduces from 17.3 ppm to 1/8 of this concentration. The [ $Te^{IV}$ ], [ $Te^{VI}$ ] and [ $Cu_2Te$ ] were calculated based on Eq. (6), (7) and (8) where  $k_1$  and  $k_2$  were 0.00754  $M^{-1}s^{-1}$  and 0.0328  $M^{-1}s^{-1}$ , respectively. Results are depicted in Figure 5.



Figure 5. Calculated  $Te^{VI}$ ,  $Te^{IV}$  and  $Cu_2Te$ concentration with time for kinetics test with  $[Cu^+]_0 =$ 0.0172 M,  $[Te^{VI}]_0 = 0.000137$  M ppm at  $T = 95.1^{\circ}C$ .

Comparison of calculated and experimental total tellurium concentration with time for the above mentioned kinetics test is shown in Figure 6.



Figure 6. Comparison of calculated and experimental tellurium concentrations with time for kinetics test with  $[Cu^+]_0 = 0.0172 \text{ M}, [Te^{VI}]_0 = 0.000137 \text{ M} \text{ at } 95.1^{\circ}\text{C}.$ 

There is suitably good agreement between the model and the experimental data. The rate constant

values were calculated accordingly for both measured and calculated tellurium concentrations via the slope of the straight lines (see Eq. (6)). The calculated rate constant considering the coupled reaction ( $k_1 =$ 0.00718 M<sup>-1</sup>s<sup>-1</sup>) was just 5% below the rate constant considering the Te<sup>VI</sup> to Te<sup>IV</sup> as a rate determining step ( $k_1 = 0.00754 \text{ M}^{-1}\text{s}^{-1}$ ). Hence, the kinetics data may be fit to a simple second order model for simplification. According to these results, a reaction mechanism can be proposed assuming the Te<sup>VI</sup> to Te<sup>IV</sup> reduction as a rate determining step.

# Conclusion

The stoichiometry of Te<sup>VI</sup> and Te<sup>IV</sup> reduction reactions with cuprous were calculated and ratios of 10:1 and 8:1 Cu<sup>+</sup> per Te<sup>VI</sup> and Te<sup>IV</sup> ion were found to be required to generate Cu<sub>2</sub>Te. Te<sup>IV</sup> reduction with Cu<sup>+</sup> is a second order reaction mechanism. first order with respect to both tellurium and cuprous concentration. Te<sup>VI</sup> reduction is four times slower than Te<sup>IV</sup> for different acid concentrations but not slow enough to be rate-determining. The significance of Te<sup>IV</sup> build-up was investigated and it was shown that the measured rate constant of the coupled reaction was just 5% below the rate constant calculated based on the assumption that Te<sup>VI</sup> reduction is rate-determining. Hence, the kinetics data can fit to a simple second order model for simplification and a reaction mechanism can be proposed assuming the Te<sup>VI</sup> to Te<sup>IV</sup> reduction as a rate determining step.

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# ENTHALPY VALUES FOR BROMINE IONS' HYDRATION IN AQUEOUS SOLUTIONS

Karpov G. V. †, Morozov I. I. \*,†, Vasiliev E. S. †, Savilov S.V. <sup>‡</sup>, Lunin V.V. <sup>‡</sup>

<sup>†</sup>Semenov Institute of Chemical Physics, Russian Academy of Sciences, Kosygin str. 4, 119991 Moscow, Russia, <sup>‡</sup>Department of Chemistry, Lomonosov Moscow State University, 119991 Moscow, Russia, <u>morozov@chph.ras.ru</u>

### Abstract

Changes of enthalpy,  $\Delta H$ , in the course of bromine ions' hydration with different number of water molecules in aqueous solutions were determined using the mass spectrographic method of electrolyte solutions electrospray in vacuum (ESESv). It was found that the Vant Hoff law holds during the addition of the two first water molecules, whereas addition of the third and fourth water molecules leads to an abrupt decrease of  $\Delta H$  and violation of the Vant Hoff law. It may be argued that the inner part of the bromine ions' hydrate shell can contain up to two water molecules. The next water molecules create the outer part of the shell, which is an intermediate structure between the structures of the inner hydrate shell and pure solvent (water).

# Keywords

hydration of bromine ions, enthalpy, electrospray, hydrate shell.

# Introduction

It is known that ions in liquid solutions are solvated and participate in all the processes occurring in electrolyte solutions precisely in such a form. Therefore, investigation of ion hydration is important for better understanding of transformation of ions in aqueous solutions (Dunsyuryun et al., 1995).

Formation of the bromine ions in water clusters has been studied in several papers. Cluster mechanism of the atmosphere ozone destruction by bromine ions was investigated by (Galashin et al., 2011). Hydrogen bond dynamics of water in NaBr solutions are studied by using ultrafast 2D IR vibrational echo spectroscopy and polarization-selective IR pump–probe experiments (Fayer et al., 2007). (Sremaniak et al., 1994) performed molecular dynamics simulations on

 $Br^-(H_2O)n$  (n=1,2 ..., 15) clusters using both a pairwise additive model and a polarizable model. They calculated the enthalpies of formation and electrostatic stabilization energies of  $Br^-(H_2O)n$  (n=1,2 ..., 15) clusters. Initial stage of formation of negative bromine ion clusters in the water has not been determined in these works. The beginning of formation the hydration shell around the bromine ion is particularly interesting.

In aqueous solution, dissociation of NaBr occurs according to scheme

 $NaBr \leftrightarrow Br - + Na^+$ 

It is followed by a process of Br- ion hydration:

$$Br^{--} + nH_2O \rightarrow (Br)^{-}(H_2O)_n (n = 1, 2, 3, 4, ...)$$

In equilibrium condition, hydration and dehydration of negative ions occur in aqueous electrolyte solutions. In

our case of the solution of bromine salts, these processes can be described by the equation:

$$Br^{-}(H_2O)_n + H_2O \leftrightarrow Br^{-}(H_2O)_{n+1}$$

According to the Vant Hoff law for electrolyte solutions in equilibrium condition, there should be a linear dependence of the logarithm of the ratio of  $Br^{-}(H_2O)_n$  to  $Br^{-}(H_2O)_{n+1}$  concentrations on the reciprocal temperature of the solution,  $T^{-1}$ . The slope of this dependence determines the value of enthalpy  $\Delta H$  during the attachment of one more water molecule to bromine ion:

$$\ln \left( I_n / I_{(n+1)} \right) = \text{Const} + (\Delta H / RT),$$

where  $I_n$  and  $I_{(n+1)}$  are the intensities of the mass spectral lines corresponding to  $Br^-(H_2O)_n$  and  $Br^-(H_2O)_n$  ions concentrations represented in n is the

 $Br^{-}(H_2O)_{n+1}$  ions concentrations, respectively; n is the number of water molecules in the hydrate shell (degree of hydration); and R is the universal gas constant.

### **Experiment and results**

Figure 1 shows the scheme of the experimental set-up. The aqueous NaBr solution was fed from the

test-tube 3 into the vacuum chamber 11 through the capillary 6 under the adjustable pressure of atmosphere air. The potential of -10 kV was applied to the capillary. When a high voltage is applied to the capillary, the electric field created on the capillary exit tip sags inside the capillary. When the solution flowing through the capillary enters this field, the ions of this solution move in such a manner, that a layer of the ions charged identically with the high voltage applied to the capillary is formed on the solution surface. The electric

potential of this layer tends to become equal to the potential of the capillary. Under the action of the surface electric field, small liquid "needles" start to stretch along the field direction. In these needles, the repulsion forces of the charges counteract surface tension forces which are proportional to the needle body radius and which keep needles' integrity. When the needle radius reaches a critical value in some place along the needle body, the tip of the needle breaks away and decomposes in explosive manner. The decomposition takes place along the surfaces which pass through the outer hydrate shells of the ions. These shells are regions of weak bond between the structure of water (solvent) and inner hydrate shells of the ions. That is why hydrated ions can emit from the solution preserving their inner hydration shells.

Pressure of ~  $10^{-5}$  Torr in the high vacuum chamber was maintained by cryogenic pumping 7 out of water at the liquid nitrogen temperature. Experimental parameters: the pressure in the vacuum chamber and the inlet orifice diameter were fixed. The ESESv mass spectra at different temperatures of electrolyte solutions were obtained with the help of an apparatus specially developed to study the enthalpy change during the successive hydration of bromine ions (Figure 1). The temperature of the copper capillary of was

maintained 5 during the experiment (Karpov, 2005, 2010). The concentration of neutralized BrNa was 0.01M. The experiments (Karpov et al., 2013)were carried out using a double focusing mass spectrograph EMAL-2 which was modified for direct sampling electrolyte solutions into the high vacuum camera. The EMAL-2 energy analyzer was tuned to transmit only the ions with the kinetic energy of 10 keV. The mass range of registered ions was 10 ÷ 300. The dynamic range of registered ion intensities was about 30. Pulsed ion current was detected using photo film UV-4. The intensities of ions were determined from the photo film blackening of corresponding mass spectral lines with the help of a MD-100 micro photometer. Eight measurements of the mass spectra were carried out. The rate of feed of the solution through the capillary varied from (~ 10<sup>-5</sup> g s<sup>-1</sup>. Under these conditions, the results were reproduced with an accuracy of ~ 15%.



Figure 1. The experimental setup: 1 inspection window; 2 - deflecting capacitor; 3 - test solution; 4 isolator; 5 - heater; 6 - copper capillary; 7 - a trap with liquid nitrogen; 8 - high voltage power supply; 9 to mass spectrograph; 10 - vacuum pump; 11 - the input diaphragm of a mass spectrograph; 12 adjustment of a solution flow.



Figure 2. Temperature dependences for hydration of bromine ions in aqueous solution NaBr 0.01 mole l<sup>-1</sup>.

The experimental data are processed by the method of ratio of averaged intensities of mass spectral peak. In and In+1 are the intensities of the mass spectral lines corresponding to the ions containing the bromine ion <sup>79</sup>Br (•) or <sup>81</sup>Br ( $\Delta$ ) and n=1 water molecules correspondingly.

	Intensity	Ion
(arbitrary units)		composition
79	47	<sup>79</sup> Br <sup>-</sup>
81	49	<sup>81</sup> Br <sup>-</sup>
97	99.5	$^{79}Br^{-}(H_2O)$
99	95	$^{81}Br^{-}(H_2O)$
115	100	$^{79}\text{Br}^{-}(\text{H}_2\text{O})_2$
117	97	$^{81}Br^{-}(H_2O)_2$
133	44	$^{79}\text{Br}^{-}(\text{H}_2\text{O})_3$
135	44	${}^{81}\text{Br}^{-}(\text{H}_2\text{O})_3$
151	16	$^{79}{ m Br^{-}}({ m H_2O})_4$
153	17	$^{81}Br^{-}(H_2O)_4$
181	36	$^{79}Br^{-}(Na^{79}Br)$
183	70	$^{79}{\rm Br}^{-}$ (Na <sup>81</sup> Br) and
165	70	$^{81}Br^{}$ (Na <sup>79</sup> Br)
185	30	$^{81}Br^{-}$ (Na $^{81}Br$ )
201	20	$^{79}Br^{-} (Na^{81}Br)(H_2O)$ and
		$^{81}Br^{-}$ (Na <sup>79</sup> Br)(H <sub>2</sub> O)

Table 1. Mass spectrum of negative ions of the aqueous solution NaBr concentration of 0.01 mol / liter at 20 C.

 $\Delta H$  values for each bromine isotope were determined:

 $Br^- + H_2O \rightarrow Br^- (H_2O)$  $\Delta H = (-6.8 \pm 0.4) \text{ kcal mole}^{-1}$ 

 $Br^-(H_2O) + H_2O \rightarrow Br^-(H_2O)_2$  $\Delta H = (-5,0 \pm 1,0)$  кcal mole<sup>-1</sup>

 $Br^- (H_2O)_2 + H_2O \rightarrow Br^- (H_2O)_3$  $\Delta H = (-1.8 \pm 0.8) \text{ kcal mole}^{-1}$ 

 ${
m Br^-} ({
m H_2O})_3 + {
m H_2O} \rightarrow {
m Br^-} ({
m H_2O})_4$  $\Delta {
m H} = (+2.0 \pm 8.8) \; {
m kcal \; mole^{-1}}$ 

The experimental results show the instability of the hydrated ion containing four water molecules.

Mass spectrum of negative charged ions of the Br consists of single ions and hydrated ions forming a Br- $(H_2O)n$  series.

The enthalpy values  $\Delta H$  at addition of the first and second water molecules to bromine ions are equal to (-28.5 ± 1.7) and (-21 ± 4.2) kJ mole<sup>-1</sup> respectively.

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# THERMODYNAMIC ASPECT: KINETICS OF THE REDUCTION OF DICYANOBIS(PHEN)IRON(III) BY ACETYLFERROCENE AND METHYLFERROCENEMETHANOL

Rozina Khattak<sup>\*1,2</sup>, Iftikhar I. Naqvi<sup>1,3</sup>

<sup>1</sup>Department of Chemistry, University of Karachi, Karachi-75270, Pakistan <sup>2</sup>Department of Biochemistry, Shaheed Benazir Bhutto Women University, Peshawar, Pakistan <sup>3</sup>Institute of Environmental Studies, University of Karachi, Karachi-75270, Pakistan

# Abstract

Protonation of acetylferrocene (FcCOMe) and  $\alpha$ -methylferrocenemethanol (FcCHOHMe) plays a vital role to lead the kinetics of the redox reactions of these organometallic compounds. Reduction of  $[Fe^{III}(phen)_2(CN)_2]^+$  by FcCOMe and FcCHOHMe exhibits this scenario. The results helped to deduce an overall second order kinetics that initially activates through a zeroth order for each reaction. The reactions follow a complex kinetic pathway as a consequence of the formation of protonated acetylferrocene (FcC<sup>+</sup>OHMe), and protonated  $\alpha$ methylferrocenemethanol (FcCHO<sup>+</sup>H<sub>2</sub>Me) in aqueous dioxane (80% v/v). A rise in the rate upon increasing concentration of protons reveals FcC<sup>+</sup>OHMe, a leading character of the rate-determining step in the reduction of  $[Fe^{III}(phen)_2(CN)_2]^+$  by FcCOMe. A reverse phenomenon during reduction of  $[Fe^{III}(phen)_2(CN)_2]^+$  by FcCHOHMe, however, helps to demonstrate participation of FcCHO+H2Me as a rate retarding entity, whilst FcCHOHMe as a species taking part in the rate-determining step. The thermodynamic parameters of activation justify the consequences by providing an authentic clue of lower activation energy and enthalpy of activation for the oxidation of acetylferrocene. The outcomes reflect the reaction hardly dependent upon temperature, and affirm involvement of highly energetic intermediate species (FcC<sup>+</sup>OHMe) in the rate-controlling step. The leading role of the neutral  $\alpha$ -methylferrocenemethanol in the rate-determining step, retardation upon its protonation, and higher values of activation energy and enthalpy of activation further affirm that the reduction of [Fe<sup>III</sup>(phen)<sub>2</sub>(CN)<sub>2</sub>]<sup>+</sup> favours by the OH containing species either FcC<sup>+</sup>OHMe derived from FcCOMe, and or FcCHOHMe itself.

# Keywords

Reduction, Kinetics, Thermodynamics, Acetylferrocene, Methylferrocenemethanol, Dicyanobis(phen)iron(III).

# Introduction

Redox reaction(s) proceed with the process of electron donation and electron acceptance between the participant reactants. Either of the two i.e., electron releasing (oxidation) or electron withdrawing (reduction) aptitude of a reactant, depends on the condition(s) in which a reaction takes place. There are several such factors that impact propensity of the chemical species and thus influence the pattern of reacBhutto Women University, Peshawar, Pakistan. Email: rznkhattak@yahoo.com

tion (R. Khattak, Naqvi, & Farrukh, 2008). The capability of electron withdrawing nature of any chemical entity is termed as, "reduction potential" and denoted by  $E_{1/2}$ . Out of a number of factors, the reduction potential of any chemical species may vary with the nature of a solvent and the electrolyte itself or a supporting electrolyte present in the vicinity (Connelly & Geiger, 1996). The mechanistic paths in an electron exchange process may thus get altered if the electron transfer takes place either in an aqueous medium or it proceeds in a pure organic solvent. These reactions could also be arranged in solvent mixtures instead. In the case it is undergone in an aqueous organic solvent mixture, a different electron exchange pathway may emerge.

<sup>• \*</sup>Dr. Rozina Khattak, Assistant Professor, Department of Biochemistry, Shaheed Benazir

Through studying the chemical kinetics and evaluating activation parameters and making the subsequent comparison, one may walk through these reaction pathways and thus, identify the major players of the mechanistic mysteries. Such investigations provide the key to elaborate scenarios regarding crucial reactions.

A few studies describe the reduction of dicyanobis(phen)iron(III) by reducing agents of biological importance such as ascorbic acid, hydroquinone, catechol, sulfatoiron and rusticyanin (Blake, White, & Shute, 1991; Matsumoto et al., 1997; Pelizzetti, Mentasti, & Pramauro, 1978; Takagi, Kagayama, Matsumoto, Tarumi, & Funahashi, 1995). These studies propose an outer-sphere mechanism for all of these reactions and estimates activation parameters for some of them. Our interest extends to determine the thermodynamic aspect of the kinetics of the reduction of dicyanobis(phen)iron(III) by acetylferrocene and  $\alpha$ -methylferrocenemethanol in aqueous dioxane. There are limited reports which approach the detailed kinetic and mechanistic analyses of the redox reactions of FcCOMe and FcCHOHMe by other transition metals or their complexes. The spectrophotometric studies are rare, however. The oxidation of acetylferrocene and a number of other derivatives of ferrocene by Cu(II) in acetonitrile yielded the reduction potential of each derivative in the particular medium by titrimetric analysis (Quirk & Kratochvil, 1970). Studies on the kinetics of the redox reactions between some ferrocene derivatives have also been published, and an outer sphere mechanism has been suggested (Pladziewicz & Espenson, 1973). Although the data is comprehensive but the study is inadequate for acetylferrocene. The data pertaining to the reactions of acetylferrocene mainly emphasize upon the synthesis of its derivatives, its role as a catalyst in the electrocatalytic oxidation of N-acetyl-lcysteine and sulfite at a glassy carbon electrode, and its electrochemical characteristics (Baciocchi, Floris, & Muraglia, 1993; Casas et al., 2007; Gao, Ma, & Liu, 2005; Gao, Zhang, & Liu, 2005; Jong, Fang, & Lin, 1999; Sasaki & Pittman, 1973; Xu, Nolan, & Cole, 1994). Meanwhile, a few reports highlight the importance and use of ferrocene-containing alcohols in chemotherapy (Osella et al., 2000; Shago, Swarts, Kreft, & Rensburg, 2007).

We frame the activity profile of FcCOMe, and FcCHOHMe by employing  $[Fe^{III}(phen)_2(CN)_2]^+$ , and highlight the important facets through determining the thermodynamic parameters of activation.

# Experimental

Analar grade chemicals were used throughout the studies. The nitrate salt of dicyanobis(phen)iron(III) was crystallized out, following the cited procedure (Schilt, 1960). The yield was purified by the procedures described (Rozina Khattak, 2011). Rapidkinetics technique helped to probe the reactions spectrophotometrically in the visible region. The highly coloured reduction product, dicyanobis(phen)iron(II);  $[Fe^{II}(phen)_2(CN)_2]$ , facilitates to ensue the reaction at 530 nm, under the condition of pseudo-first order. The concentration of reductants was always in excess over oxidant. The plots were always linear and the results were coherent to the integrated rate equations of different orders. The datum points are the average of 3-6 readings.

# **Results and Discussion**

### Kinetic Parameters

To determine the order of reaction with respect to  $[Fe^{III}(phen)_2(CN)_2]^+$ , the change in absorbance corresponding to time, was measured. The integrated rate equations of zeroth and first order cohered the data. This reactivity pattern substantiates a complex kinetics with respect to [Fe<sup>III</sup>(phen)<sub>2</sub>(CN)<sub>2</sub>]<sup>+</sup>. The rate of the reactions followed a zeroth order in the primary stage. The first order kinetics leads the rate soon after first zone, and the rate of insolubility of  $[Fe^{II}(phen)_2(CN)_2]$  and rate of reactions compete each other in the subsequent region to the end of reactions. A plot of absorbance versus time yields the product of molar absorptivity of  $[Fe^{II}(phen)_2(CN)_2]$  ( $\epsilon$ ) and the zeroth order rate constant ( $k_{obs}$ ) with the dimension,  $s^{-1}$ . This value is  $\varepsilon$  times greater than  $k_{obs}$ . The property ' $\varepsilon$ ' carries a constant value, which doesn't interrupt the impact of any parameter on  $k_{obs}$ . The plot of ln absorbance and time as y-x coordinates respectively, vields  $k'_{obs}$  as a slope with a dimension (s<sup>-1</sup>).  $k'_{obs}$ represents the pseudo-first order rate constant.

The values of the rate constants,  $\epsilon k_{obs}$  and  $k'_{obs}$ , for each reaction don't show any alteration upon increasing or decreasing the concentration of  $[Fe^{III}(phen)_2(CN)_2]^+$  keeping [FcCOMe] or [FcCHOHMe], temperature, ionic strength, dielectric constant and pH fixed (Figure 1). This behaviour justifies the composition(s) of the reaction mixture(s) to be appropriate for pursuing the reaction under pseudo-first order condition.



Figure 1. Kinetic data with respect to  $[Fe^{III}(phen)_2(CN)_2^+]$ . The experimental conditions were maintained at 0.18 mM (ionic strength, I), 80% v/v aqueous-dioxane, 304 ± 0.5 K (for FcCOMe) and 291 ± 0.5 K (for FcCHOHMe). The circle and triangle represent the effect of variation in the concentration of  $[Fe^{III}(phen)_2(CN)_2]^+$  on  $\varepsilon k_{obs}$  ( $\Delta$ ), and  $k'_{obs}$  ( $\circ$ ) at 1.3 mM [CpCOMe]. The square and dash show the impact on  $\varepsilon k_{obs}$ ;  $\Box$ ,  $k'_{obs}$ ; -, at 1.3 mM [FcCHOHMe].

The effect of variation in the concentration of FcCOMe or FcCHOHMe remains neutral on ' $\varepsilon k_{obs}$ ', at constant  $[Fe^{III}(phen)_2(CN)_2^+]$  and other parameters. The value of  $k'_{obs}$  increases in both cases. This rise in the figure is linear in case of FcCHOHMe, whilst the linearity bent at higher concentrations of FcCOMe. The results elaborate an initial zeroth order with respect to FcCOMe or FcCHOHMe, and a first order The ascending corresponding to FcCHOHMe. curvature indicates the first order kinetics with respect FcCOMe, and reveals involvement of an to intermediate in the rate-determining step. The bending curvature also demonstrates the role of certain reacting entity as a limiting reactant. The activity profile for each reaction is mentioned in Figure 2.



Figure 2. Effect of [FcCOMe] and [FcCHOHMe] on  $(\varepsilon k_{obs}; \Delta, k'_{obs}; \circ)$  and  $(\varepsilon k_{obs}; \Box, k'_{obs}; -)$ , respectively. The experimental conditions were fixed at 0.075 mM [Fe<sup>III</sup>(phen)<sub>2</sub>(CN)<sub>2</sub>]<sup>+</sup>, 0.18 mM (I), 80% v/v aqueousdioxane, 304 ± 0.5 K (for FcCOMe) and 291 ± 0.5 K (for FcCHOHMe). The filled circle and dash mention  $k'_{obs}$  at 1:1 concentration ratio between oxidant and reductant.

Protonation is a well known characteristic of carbonyl group in any compound. This facet is prominent in acetylferrocene (FcCOMe) and  $\alpha$ -methylferrocenemethanol (FcCHOHMe), and plays a leading role in the redox reactions of these organometallic compounds. We probed our targeted reactions in aqueous dioxane, which facilitates hydrogen bonding and produce acidic character in the medium. This acidity provides a base to the protonation of FcCOMe and FcCHOHMe at oxygen atom. The protons bond to electron rich oxygen atoms, and

produce monopositive protonated compounds such as FcCO<sup>+</sup>HMe and FcCHO<sup>+</sup>H<sub>2</sub>Me. The protonated acetylferrocene is stabilized by resonance, and yields an unsaturated compound with a carbonium atom, FcC<sup>+</sup>OHMe. This scenario is affirmed, while the influence of increasing concentration of protons on the rate constants is studied. In case of the reduction of  $[Fe^{III}(phen)_2(CN)_2]^+$  by FcCOMe the rate accelerates  $(k'_{obs} \text{ increases})$ , and slowdowns  $(k'_{obs} \text{ decreases})$  in the reaction of FcCHOHMe. The zeroth order rate constant remains unaffected in each case. The results have been illustrated in Figure 3. Such conduct confirms participation of protonated acetylferrocene and  $\alpha$ methylferrocenemethanol in the mechanistic pathways of the reactions. The bending curvatures at higher concentrations of protons demonstrate FcCOMe or FcCHOHMe as the limiting reactants. The rate enhancing profile confirms FcC<sup>+</sup>OHMe as the reactive entity that takes part in the rate-determining step, and leads the rate through first order. The zeroth order, however, involves unprotonated FcCOMe. Meanwhile, the rate decelerating aspect upon protonation of FcCHOHMe substantiates FcCHO+HMe to donate electron through zeroth order kinetics, and FcCHOHMe via first order. This also supports the characteristic of  $\alpha$ -methylferrocenemethanol as the rate regulating entity, which takes part in the ratedetermining step.



Figure 3. Effect of protons on the rate constants ( $\varepsilon k_{obs}$ ;  $\Delta$ ,  $k'_{obs}$ ;  $\circ$ ) of [FcCOMe] and ( $\varepsilon k_{obs}$ ;  $\Box$ ,  $k'_{obs}$ ; -) of [FcCHOHMe]. The experimental conditions were maintained at 5.1 mM (I), 0.075 mM ([Fe<sup>III</sup>(phen)<sub>2</sub>(CN)<sub>2</sub>]<sup>+</sup>) and 0.751 mM ([FcCOMe] or ([FcCHOHMe]).

### Thermodynamic Parameters of Activation

The reactions were probed at different temperatures to evaluate the thermodynamic parameters of activation. Any variation in temperature doesn't bring any change in the values of  $\varepsilon k_{obs}$  for the two reactions. The figure of  $k'_{obs}$  increases in both cases. The activation energy ' $E_A$ ' and 'A' factor of the redox reactions were estimated from the values of the slope and intercept, respectively, by drawing a graph of,  $lnk'_{obs}$  versus 1/T, according to the Arrhenius

equation. The values of the thermodynamic parameters of activation such as, enthalpy and entropy of activation ( $\Delta H^{\#}$ ,  $\Delta S^{\#}$ ) were determined by plotting, *ln* ( $k'_{obs}/T$ ) vs 1/T, according to the Eyring equation. The Gibbs energy of activation ( $\Delta G^{\#}$ ) was then calculated by employing equation,  $\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$ . These estimated figures of  $E_A$ , A,  $\Delta H^{\#}$ ,  $\Delta S^{\#}$  and  $\Delta G^{\#}$  have been displayed in Table 1.

The redox reactions between  $[Fe^{III}(phen)_2(CN)_2]^+$  and FcCOMe, and or, FcCHOHMe were found to conform to the provision of transition state theory. The +ve figure(s) obtained for the enthalpy of activation ( $\Delta H^{\#}$ ) and Gibbs free energy of activation ( $\Delta G^{\#}$ ) classify the reaction to be taken as endothermic. The rates of reactions were accordingly observed to increase upon increasing the temperature.

The electrostatic term of the equation of the rate constant, based upon transition state theory, predicts the nature of involved charges and the solvent interaction with the species of the reaction while forming the activated complex. A smaller value of  $\Delta H^{\#}$  with a loss of entropy  $\Delta S^{\#}$  (larger –ve numeral) suggests that the reacting entities carry like charges demonstrating a characteristic associative mechanism. However a reverse case, the +ve contribution to  $\Delta H^{\#}$  with a gain in entropy  $\Delta S^{\#}$  (smaller –ve numeral) is observed for unlike charges with an associative mechanism.

Table 1. Thermodynamic parameters of activation.

	FcCOMe	FcCHOHMe
$E_{\rm A}$ (kJ mol <sup>-1</sup> )	11.41	27.7
$\begin{array}{c} A \\ (\mathrm{s}^{-1}) \end{array}$	369	337055
$\Delta H^{\#}$ (kJ mol <sup>-1</sup> )	8.83	25.3
$\Delta S^{\#}$ (J mol <sup>-1</sup> K <sup>-1</sup> )	-204.45	- 147
$\Delta G^{\#}$	70.6	69.7
(kJ mol <sup>-1</sup> )	at 302 K	at 302 K

A close examination of the thermodynamic parameters of activation (Table 1) helps to demonstrate small  $E_A$ ,  $\Delta H^{\#}$  and  $-\text{ve }\Delta S^{\#}$  value(s) to be a characteristic representative of an associative mechanism in case of acetylferrocene. This provides a strong support to the electron donating facet of FcC<sup>+</sup>OHMe in the rate-determining or slow step. This has already been discussed that the unsaturated protonated acetylferrocene is highly energetic and reactive. It means that the monopositive species needs small quanta of energy to cross the barrier of activation energy to yield products. We observed this in our study. A low value of the enthalpy of activation reinforces our findings. Contrary to that, we observed normal and reasonable values of  $E_A$ ,  $\Delta H^{\#}$  and  $-\text{ve }\Delta S^{\#}$ during the reduction of dicyanobis(phen)iron(III) by  $\alpha$ methylferrocenemethanol because of the reactivity of saturated and stable species FcCHOHMe in the rate-determining step.

# Conclusion

The result obtained from the kinetic data and its thermodynamic aspect refer to the existence of an equilibrium among the deprotonated and protonated acetylferrocene, and or,  $\alpha$ -methylferrocenemethanol. Two species of each organometallic compound take part in the electron exchange reaction, and donate electron to [Fe<sup>III</sup>(phen)<sub>2</sub>(CN)<sub>2</sub>]<sup>+</sup>. Protonation of FcCOMe to yield a conjugate acid; FcC+OHMe in acidic medium is well known (Arnett & Bushick, 1962; Rubalcava & Thomson, 1963). Our investigation provides an evidence that the oxidation of FcCOMe and FcCHOHMe is controlled by the OH containing entity either saturated at carbon center or unsaturated at acetyl group. The study further evinces that in biochemical reactions or other processes, it is crucial to consider the rate-regulating role of such species.

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# KINETIC STUDIES IN MICELLAR SYSTEMS UNDERGOING MORPHOLOGICAL TRANSITIONS

<u>Pilar López-Cornejo</u><sup>\*</sup>, Manuel López-López<sup>†</sup>, Beatriz Sarrión, Francisco J. Ostos and María Luisa Moyá University of Seville and <sup>†</sup>University of Huelva- Spain

# Abstract

At concentrations above the critical micelle concentration, cmc, surfactants tend to self-associate in water to form micelles whose characteristics depend on surfactant nature as well as on temperature. Additives affect the selfaggregation process and the features of the formed aggregates. This influence operates through variations in the chemical potential of the surfactant molecules in the bulk phase,  $\mu^{o}_{surfactant}$  (bulk), as well as in the chemical potential of the surfactant molecules in the micelles,  $\mu^{o}_{surfactant}(m)$ . The importance of one or another effect depends on the nature of the additive. The changes caused by the additives can be made evident through the study of adequately chosen chemical reactions in the micellar solutions. Since the process between methyl naphthalene-2-sulfonate, MNS, and bromide ions meets the requirements, this process was investigated in alkanediyl- $\alpha$ - $\omega$ -bis(dodecyldimethylammonium) bromide, 12s-12,2Br, micellar solutions in the absence and in the presence of various additives. The additives used were the polar organic solvent 1,2-propylene glycol, which remains in the bulk phase, 1-butanol, that distributes between the bulk and micellar pseudophases, and the surfactant N-decyl N-methylglucamide, MEGA10, which forms mixed micelles with the gemini surfactants. Many of these micellar solutions undergo morphological transitions when surfactant concentration increases, the micelles changing shape from spherical aggregates into elongated ones. The surfactant concentration at which this morphological transition occurs is often referred to as second cmc ( $C^*$ ). The sphere-to-rod transition is followed by variations in the characteristics of the micellar aggregates which will affect the rate of the MNS + Br<sup>-</sup> process.

In this work, a new kinetic treatment was developed in order to quantitatively rationalize the kinetic micellar effects observed in the whole surfactant concentration range, below and above the morphological transition. This treatment was also shown to be useful in the presence of the additives which, not only alter the aggregation process, but also the surfactant concentration range in which the spherical-to-rod transition takes place. To the authors' knowledge, this is the first attempt at quantitatively explaining the kinetic micellar effects caused by the changes in the micelles characteristics accompanying morphological transitions.

# Keywords

Kinetics, dimeric micelles, surfactants, ethylene glycol, alcohols, morphological transitions.

# Introduction

Surfactants are surface active compounds that decrease interfacial tension or interfacial Gibbs energy of interfaces. They have distinctly separate hydrophilic and hydrophobic parts and their importance in practical applications continues to grow. They are used in antibacterial compounds, liquid crystals, oil recovery, mineral flotation, and other aspects of material science (Karsa, 1990). Surfactants commonly show selfassembly, resulting in different structures such as micelles, vesicles, etc. Micelle formation is governed by a balance among several factors, e.g., the relative sizes of the hydrophilic and hydrophobic parts, the presence of charges, and the degree of hydration, but it generally occurs at a well-defined concentration, the critical micelle concentration (cmc). Additives affect the self-aggregation process and the features of the formed aggregates. This influence operates through variations in the chemical potential of the surfactant molecules in the bulk phase,  $\mu^{o}_{surfactant}(bulk)$ , as well as in the chemical potential of the surfactant molecules in the micelles,  $\mu^{o}_{surfactant}(m)$ . The importance of one or

another effect depends on the nature of the additive. Some micellar aggregates present the additional interest of undergoing morphological transitions when surfactant concentration increases. So, micelles formed by several gemini surfactants change their shape from spherical into elongated aggregates. The surfactant concentration at which this morphological transition occurs is often referred to as "second cmc" (C\*) (Zana, 2002). These transitions are accompanied by changes in the micelles properties. These changes can be make evident through the kinetic study of adequately chosen chemical reactions. Bearing this in mind, the occurrence of morphological changes in the micellar aggregates formed bv alkanedyil- $\alpha, \omega$ bis(dimethyldodecylammonium) bromide, 12-s-12,2Br- ( s=2,3,4,5,6,8,10,12), upon increasing [surfactant], in the presence and in the absence of additives such as 1,2-propylene glycol, N-decyl Nmethyl-

<sup>\*</sup>To whom all correspondence should be addressed (pcornejo@us.es)

glucamide (MEGA10) and 1-butanol, have been studied by investigating the kinetic micellar effects on the  $S_N2$  substitution reaction between methyl naphthalene-2-sulfonate (MNS) and the bromide surfactant counterions (Br<sup>-</sup>).

# Experimental

MEGA10, and 1-butanol were from Fluka and used without further purification. Propylene glycol was from Aldrich. MNS was synthesized following the method in the literature (Bacaloglu, R. et al., 1989). The surfactants were synthesized as is indicated in Menger, F.M. et al., 2000, and characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR and elemental analysis. The reaction MNS + Br-(scheme 1) was recorded at 326 by using a Hitachi 3100 and а Shimadzu 1800 UV-visible spectrophotometers. The bromide ions involved in the process come from the surfactant molecules and no additional Br- was added.





### **Results and Discussion**

Figure 1 shows the influence of the dimeric surfactant concentration [12-3-12,2Br<sup>-</sup>] on the process MNS + Br-. Similar behaviours were observed for all the surfactants. The two reagents, MNS and Br-, are distributed between the bulk and micellar pseudophases. Therefore, the process is taking place simultaneously in the two pseudophases and the reaction rate is the sum of the two contributions. An increase in surfactant concentration brings about a further incorporation of the organic substrate molecules into the micelles. As a consequence, the contribution of the reaction occurring in the micellar pseudophase increases and, given that the bromide ion concentration in the pseudophase is much higher than that in the bulk phase, the observed rate constant augments. For a process of this type, the kobs can be written as (Romsted et al., 1997):

$$\mathbf{k}_{obs} = \frac{\mathbf{k}_{2}^{w} [\mathbf{B} \mathbf{r}_{w}^{-}] + (\mathbf{k}_{2}^{m} / \mathbf{V}_{m}) [\mathbf{B} \mathbf{r}_{m}^{-}] \mathbf{K}_{m}}{1 + \mathbf{K}_{m} [\mathbf{12} - \mathbf{s} - \mathbf{12}, \mathbf{2B} \mathbf{r}_{m}^{-}]} = \frac{\mathbf{k}_{2}^{w} [\mathbf{B} \mathbf{r}_{w}^{-}] + \mathbf{k}_{2m} [\mathbf{B} \mathbf{r}_{m}^{-}] \mathbf{K}_{m}}{1 + \mathbf{K}_{m} [\mathbf{12} - \mathbf{s} - \mathbf{12}, \mathbf{2B} \mathbf{r}_{m}^{-}]}$$
(1)

Here  $[Br_w]$  and  $[Br_m]$  are the bromide ion concentrations in the aqueous and micellar pseudophases, referred to the total solution volume.  $V_m$ is the molar volume of the reactive region at the micellar surface and  $K_m$  is the equilibrium binding constant of the MNS molecules to the dimeric micelles.  $[12-s-12,2Br_m]$  is the micellized surfactant concentration.  $k_2^w$  and  $k_2^m$  are the second order rate constants in the aqueous and micellar pseudophases (in mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>), respectively, and  $(k^m_2/V_m)=k_{2m}$  (in s<sup>-1</sup>) is the second order rate constant in the micellar pseudophase written with the concentrations expressed as molar ratios,  $[Br^-_m]/[12-s-12,2Br^-_m]$ . The bromide ion concentrations in the aqueous and micellar pseudophases can be estimated by using eqs. 2 and 3

$$[\mathbf{Br}_{\mathbf{m}}] = \alpha [12 - \mathbf{s} - 12, 2\mathbf{Br}_{\mathbf{m}}]$$
(2)

$$\begin{bmatrix} \mathbf{B}\mathbf{r}_{w}^{-} \end{bmatrix} = \begin{bmatrix} 12 - s - 12, 2\mathbf{B}\mathbf{r}_{\text{Total}}^{-} \end{bmatrix} - \begin{bmatrix} \mathbf{B}\mathbf{r}_{m}^{-} \end{bmatrix}$$
(3)

where  $\alpha$  is the micellar ionization degree. Eq. 1 considers  $\alpha$  constant in the whole surfactant concentration range. The dotted line in Figure 1 is the



result of fitting the kinetic data by using eq. 1. One can see that the trend in kobs cannot be explained by using this eq.. If changes in  $\alpha$  accompanying the morphological transition are taken into account in eq. 1, the dash-dot-dot line was obtained. The agreement between the theoretical and the experimental data has improved, but it is not good. This could be due to the fact that micellar growth causes other changes in the aggregate characteristics that have been not taken into account in eq. 1. Micellar growth is accompanied by changes in the micropolarity of the interfacial region (Graciani et al., 2010), in  $V_m$  and in the interfacial water content (Geng et al., 2006). As a consequence, for [surfactant]> $C^*$ ,  $K_m$  and  $k^m_2$  can vary upon increasing surfactant concentration. In order to quantitatively rationalize the kinetic micellar effects within the whole surfactant concentration range investigated, eq. 4 will be used:

$$k_{obs} = \frac{k_2^w [Br_w] + k_{2m} [Br_m] K_m}{1 + K_m [12 - s - 12, 2Br_m]} + b [12 - s - 12, 2Br_m]^2$$
(4)

where *b* can be considered as an *empirical parameter*. In order to understand the meaning of *b* one has to consider that micelles influence the rates of micellemodified reactions through two different effects: i)The *concentration effect*, which results from the concentration or depletion of reactants in the interfacial region and has a major effect on the rates of bimolecular processes (such as MNS + Br<sup>-</sup>). ii)The *medium effect*, which depends on the transfer of substrate from water to micelles, on the reaction mechanism, and on the properties of the interfacial region, such as local charge, polarity and water content. Usually, the kinetic micellar effects observed in bimolecular processes are mainly due to the concentration effect. However, there are processes for which large kinetic micellar effects, not connected to concentration effects, are operative (Rodríguez et al., 2001). The difference between  $k_{2}^{w}$  and  $k_{2}^{m}$  would account for the micellar medium effects when no morphological transitions occur. Since in eq. 4 the changes in the micellar ionization degree caused by the micellar growth were taken into account, the value of bincludes the medium micellar effects caused by the changes in the aggregate characteristics following micellar growth. Figure 1 also shows the good fit of the k<sub>obs</sub> values obtained by using eq. 4.

As was previously mentioned, the presence of additives alters the second cmc. The effects produced depend on the characteristics of the additive. Here different additives have been used: propylene glycol, 1butanol and MEGA 10. Propylene glycol remains in the bulk phase, lowering its polarity and making it a better solvent for the surfactant molecules. This produces an increase in the cmc and C\*, a decrease in the aggregation number and an increment in the micellar ionization degree. MEGA 10 molecules forms mixed micelles with the dimeric surfactants. Its presence causes a diminution in the electrostatic repulsions between the charged head groups and, therefore, an increase in the micellar ionization degree. On the other hand, 1-butanol is distributed between the aqueous and the micellar pseudophases. The intercalation of alcohol molecules into the dimeric micelles diminishes the electrostatic repulsions between the positively charged head groups, promoting micellization and reducing the electrostatic charge density at the interfacial region. All these changes in the micellar systems provoke changes in the rate constant of a chemical process.

The expression for the observed rate constant depends on the nature of the additive. When an organic polar solvent, such as propylene glycol, is added to the aqueous micellar solution one can write:

$$k_{obs} = \frac{k_2^{bulk} [Br_{bulk}] + k_{2m} [Br_{m}] K_{m}}{1 + K_{m} [12 - s - 12, 2Br_{m}]} + b \left[ 12 - s - 12, 2Br_{m} \right]^2$$
(5)

Here the different terms have the same meaning as in eq. 4. In this case, the authors used the term *bulk* phase instead of aqueous phase in order to consider that now the bulk phase is a water- propylene glycol binary mixture, with a determined weight percentage of the alcohol. The solid line in Figure 2 shows that, for 10% wt of propylene glycol, the agreement between the theoretical and the experimental data by using eq, 5 is good. In the case of 30% wt of organic solvent no morphological transition is observed for [12-5-12,2Br] < 0.1 M. In this case, eq. 1 is expected to be able to fit quantitatively the kinetic data.

For dimeric-MEGA10 mixed micellar solutions the observed rate constant can be written:

$$\mathbf{k}_{obs} = \frac{\mathbf{k}_{2}^{w} [\mathbf{B} \mathbf{r}_{w}^{-}] + \mathbf{k}_{2m} [\mathbf{B} \mathbf{r}_{m}^{-}] \mathbf{K}_{m}}{1 + \mathbf{K}_{m} [\mathbf{Surfactant}_{m}]} + \mathbf{b} [\mathbf{Surfactant}_{m}]^{2}$$
(6)

where the terms have the same meaning as in eq. 4 and m refers to the micellar pseudophase of the mixed micelles. Figure 3 shows that eq. 6 can fit reasonable well the kinetic data observed in 12-2-12,2Br-MEGA10 mixed micellar solutions with  $X_{dimeric}=0.9$ .



In water-1-butanol dimeric micellar solutions the observed rate constant can be expressed as:

$$\mathbf{k}_{\text{ts}} = \frac{\mathbf{k}_{2}^{\text{buik}} |\mathbf{B}_{\mathbf{T}_{\text{buik}}}| + \mathbf{k}_{2m} |\mathbf{1}_{2} - \mathbf{s}_{-12,2} \mathbf{B}_{\mathbf{T}_{m}}^{-1} |\mathbf{B}_{\mathbf{T}_{m}}^{-1} |\mathbf{K}_{m}}{(\mathbf{1} + \mathbf{K}_{m} [\mathbf{1}_{2} - \mathbf{s}_{-12,2} \mathbf{B}_{\mathbf{T}_{m}}^{-1}])([\mathbf{1}_{2} - \mathbf{s}_{-12,2} \mathbf{B}_{\mathbf{T}_{m}}^{-1}] + [\mathbf{A}_{1\text{cohols}}])^{+b} [\mathbf{1}_{2} - \mathbf{s}_{-12,2} \mathbf{B}_{\mathbf{T}_{m}}^{-1}]}$$
(7)

The terms have the same meaning as in eq. 4. Given that 1-butanol molecules distribute between the micellar and aqueous phases, the authors prefer the term *bulk* phase in order to point out that the continuous phase is a water-1-butanol mixture. The term  $[12-s-12,2Br_m]+$  [alcohol<sub>m</sub>] takes into account that incorporation of alcohol molecules into the micelles will increase the concentration of the micellar pseudophase, which is equivalent to *diluting* micellar bound reactants. In order to estimate [alcohol<sub>m</sub>], the distribution of the alcohol molecules between the micellar and bulk (water-alcohol) phases was described by using eq. 8:

$$K = \frac{[Alcohol_{T}] - [Alcohol_{w}]}{[Alcohol_{w}] ([Surfactant_{w}] + [Alcohol_{T}] - [Alcohol_{w}])}$$
(8)

where K is the distribution coefficient, and subscripts T, m and w refer to the total, micellar and aqueous alcohol concentrations referred to the total solution

volume. The authors considered a value of K=1 mol  $dm^{-3}$  for 1-butanol in the dimeric micellar solutions at 303 K, with the dimeric surfactant concentration in eq. 8 expressed per surfactant tail chain. It is worth noting that application of eq. 8 in the whole surfactant concentration range means that variations in the shape and size of micelles do not affect their solubilization capacity. Therefore, the alcohol concentrations estimated are approximate. The solid line in Figure 4 shows that the experimental kinetic data can be adequately explained by using eqs. 7 and 8.



Figure 4

K<sub>m</sub> values obtained from the fittings show that addition of propylene glycol, MEGA10 and 1-butanol results in a decrease in the equilibrium binding constant. The presence of the additives does not seem to affect  $k_{2m}$  substantially. With regard to the *b* values, they follow the opposite trend shown by the second cmc. That is, when the presence of an additive causes an increment in  $C^*$ , b decreases. An increase in  $C^*$ , for a given dimeric surfactant, can be taken as indicative that the tendency to micellar growth upon increasing surfactant concentration decreases. As a consequence, changes in [surfactant] will cause a less pronounced variation in the characteristics of the interfacial region and, as a result, the medium kinetic micellar effects are also expected to decrease. Therefore, a decrease in b would be expected, as observed.

On the basis of the meaning proposed by the authors for b, the variations observed in this parameter in the presence of the different additives investigated are reasonable. It is also consistent with the results obtained for the aqueous dimeric micellar solutions. Therefore, in spite of the approximations, the fitting method developed in this work in order to quantitatively discuss the kinetic data in the whole surfactant concentration range seems meaningful.

# Conclusions

The reaction methyl naphthalene-2-sulfonate + Br<sup>-</sup> was investigated in several alkanediyl- $\alpha$ - $\omega$ bis(dodecyldimethylammonium) bromide, 12-s-12,2Br<sup>-</sup>

(with s=2, 3, 4, 5, 6, 8, 10, 12) micellar solutions in the absence and in the presence of various additives. The additives were 1,2-propylene glycol, which remains in phase, N-decyl N-methylglucamide, the bulk MEGA10, which forms mixed micelles with the dimeric surfactants, and 1-butanol, which distributes between the aqueous and micellar phases. In all cases, with the exception of water- propylene glycol with 30% by weight of organic solvent, 12-5-12,2Brmicellar solutions undergo a sphere-to-rod transition upon increasing surfactant concentration. The kinetic data within the whole surfactant concentration range have been quantitatively explained by considering a modification of the pseudophase model. The decrease in the micellar ionization degree accompanying micellar growth, which accounts for the concentration micellar kinetic effects caused by the sphere-to-rod transition, was taken into account. Besides, an additional term including the medium micellar kinetic effects coming from micellar growth has also been considered.

It is the first time, to the authors' knowledge, that kinetic micellar effects on a micelle-modified reaction have been quantitatively explained in a micellar reaction media where a morphological transition occurs.

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# EFFECTS OF AXIAL LIGANDS ON THE FORMATION KINETICS OF WATER-SOLUBLE SAMARIUM(III) PORPHYRINS

Melitta Patrícia Kiss\*, Zsolt Valicsek and Ottó Horváth Department of General and Inorganic Chemistry, Institute of Chemistry, Faculty of Engineering, University of Pannonia Egyetem str. 10., Veszprém, H-8200, Hungary

# Abstract

Presence of potential axial ligands can accelerate the coordination of the first porphyrin, but it can hinder the connection of a further porphyrin to the metal center. Coordination of the first monodentate ligand (chloride or ethanol) results already in the acceleration; however, in the case of a bidentate one (acetate or glycol), deceleration takes place. The steric effect (change in the coordination number) of the second bidentate ligand is necessary, too.

# Keywords

out-of-plane metalloporphyrins, lanthanide(III) ions, axial enhancement or hindrance, spectrophotometry, oligomerization

# Introduction

Lanthanide(III) ions offer good opportunities to examine the special properties of out-of-plane (OOP or sitting-atop=SAT) metalloporphyrins, utilizing the well-known lanthanide contraction. Their insertion into the coordination cavity of porphyrin ligand is a slow and complicated process in aqueous solution, originating from the high stability of their aqua complexes and oligomer forms. As a consequence of the lanthanide(III) ions' Pearson-type hard character, they can coordinate rather to the peripheral substituent of porphyrin, if it possesses similarly hard O-donor atom (e.g. carboxy-, sulfonato-phenyl). Only under thermodynamic control, at higher temperatures, can coordinate the metal ion also, or rather, to the four pyrrolic nitrogens; resulting in the formation of typical metalloporphyrin complexes (Kiss et al., 2014).

Moreover, they incline to higher coordination number (8-12), which can materialize in their sandwich complexes, owing to the simultaneous coordination of two tetradentate porphyrin ligands to a metal center (Valicsek et al., 2012).

# Results

In this work, we investigated the potential effects of various axial ligands on the reaction between the anionic 5,10,15,20-tetrakis(4-sulfonatophenyl) porphyrin and samarium(III) ion, as the sixth member of the lanthanide series. Any potential axial ligand can enhance the coordination of the first porphyrin ligand, but it can hinder the connection of a further porphyrin (Wong et al., 2007).

\* Corresponding author:

kiss.melitta.p@gmail.com

Insertion of these larger metal ions into the porphyrin cavity can be spectrophotometrically followed due to the redshifts of UV-Vis, intraligand  $\pi\pi^*$  absorption bands, similarly to other typical OOP complexes, which display "common" absorption properties (Valicsek et al., 2013).



Figure 1. Soret-absorption spectral changes during the reaction between 1.2×10<sup>-2</sup> M Sm<sup>3+</sup> and a) 1.0×10<sup>-6</sup> M H<sub>2</sub>P<sup>4-</sup> (at 65 °C) in the presence of 1 M NaAc/HAc buffer (pH=6), reaction total time: 15 h.
b) 7.1×10<sup>-7</sup> M H<sub>2</sub>P<sup>4-</sup> (at 65 °C) in the presence of 0.1 M NaCl and NaClO<sub>4</sub> (1 M ionic strength), total time: 56 h.

If non-coordinating perchlorate ion is applied to adjust the ionic strength, samarium(III) bisporphyrin can form too, which has slightly further redshifted and broadened absorption bands, compared to those of the monoporphyrin (Fig. 1. a-b). As a consequence of this small difference between the molar absorption spectra of the metallo-mono- and bisporphyrin, the formation of the latter is indicated only by the decrease of absorbances at nearly the same wavelengths (421 nm in Fig. 1.b). Furthermore, the reaction slows down: 56 hours is not enough to reach the equilibrium, while in the presence of acetate ~8 hours proved to be sufficient (Fig. 1.a) at the same concentrations, ionic strength, pH, and temperature.

During a deeper investigation of this phenomenon, low (0.01 M) acetate concentration was enough to totally hinder the formation of bisporphyrin. In this concentration range the partial molar fraction of monoacetato-lanthanide(III) complexes,  $[LnAc]^{2+}$ , began to increase. Simultaneously, the apparent (calculated for the total, initial metal ion concentration) formation rate constant of the porphyrin complex decreases; the acceleration is observable only at somewhat higher acetate concentration (Fig. 2), together with the appearance of diacetato complexes, [LnAc<sub>2</sub>]<sup>+</sup>. The coordination number may change from 9 (in the initial nonaaqua complex, which is characteristic of the early lanthanide ions) to 8, and this latter one fits better to the insertion into the porphyrin's cavity, resulting in the SAPR-8 (square antiprism) or CU-8 (cubic) coordination polyhedron. Finally, at higher acetate coordination, the formation of triacetatolanthanide(III) complex, [LnAc<sub>3</sub>], can slightly decelerate again the insertion into the macrocycle, as a consequence of the steric hindrance of the third, bidentate ligand (Fig. 2, Kiss et al., 2014).



Figure 2. Change of the apparent formation rate constant of samarium(III)-monoporphyrin with the increase of acetate concentration.

In the presence of a neutral bidentate ligand, e.g., glycol, instead of the anionic acetate, the charge of the complex forms of metal ion does not change during the ligation; hence, their activity coefficient may have no additional accelerating effect on the insertion into the porphyrin cavity. In the case of monodentate ligands, chloride or ethanol, already the coordination of the first one enhances the metalation of porphyrin, due to their trans effect. The negative charge of chloride increases the activity coefficient, similarly to acetate. However, on the basis of our experiments, the coordination of potential axial ligands to a lanthanide ion may result in steric, rather than electronic effects on the formation of the metalloporphyrin. The latter ones as trans-effects (acceleration of the solvent molecule's exchange reaction in the opposite coordination position) were mainly referred to in the case of transition and posttransition metal ions in the literature (Valicsek et al., 2013).

# Conclusions

As a conclusion, we can declare that it would be necessary to separately determine the electronic and steric effects of the axial ligand(s) on the formation of metalloporphyrins. The first step is that also the changes in the activity coefficients of metal complexes should be taken into consideration.

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# THE ROLE OF WATER AND THE LIGAND'S CHARGE IN THE FORMATION KINETICS OF BISMUTH(III) PORPHYRINS

Zsolt Valicsek<sup>\*,a</sup>, Katalin Patonay<sup>a,b</sup> and Ottó Horváth<sup>a</sup>

a) Department of General and Inorganic Chemistry, Institute of Chemistry, University of Pannonia, Egyetem str. 10, Veszprém, H-8200, Hungary; <u>valicsek@vegic.uni-pannon.hu</u> b) Egerfood Knowledge Center, Leányka str. 6/D, Eger, H-3300, Hungary

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The formation of metalloporphyrins in aqueous solution (or in other polar solvents) is an equilibrium reaction, owing to the higher activity and mobility of metal ions than in nonpolar solvents. In the reaction between extremely large metal ions (e.g.  $Tl^+$ ,  $Pb^{2+}$ ,  $Bi^{3+}$ ) and porphyrins, the end-product in apolar solvents may possess highly redshifted absorption bands because, as a consequence of the large out-of-plane distance of the metal center, a ruffled-like deformation of the periphery may superpose on the highly dome-distorted structure. Considering the bathochromic or (not quite correctly) hyperchromic effect, the complexes possessing so highly redshifted absorption bands used to be called as hyper-porphyrins. However, these species are only intermediates in aqueous solutions [1]. The absorption spectrum of the transformation reactions' end-products in water is very similar to those of the appreciable coordination ability or the polarizing effect of water molecules (and the ionic ligand), which can promote the complex to overcome the kinetic energy barrier toward the more stable structure, in which the metal center is located closer to the ligand plane, resulting in the decrease of distortion as well as that of the redshift.

The amount of the intermediate complex in water is negligible in the case of thallium(I), considerable in the case of bismuth(III), and dominant in the case of lead(II) because its transformation reaction is very slow. Therefore in this work, we studied the reaction between bismuth(III) and the anionic 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin as well as the cationic 5,10,15,20-tetrakis(1-methyl-4-pyridinium)porphyrin. The intermediate complex was shorter-lived in the case of anionic porphyrin, and more long-lived with cationic one; probably as a consequence of the positive charge on the ligand repulsing the metal ions.

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