## 11<sup>TH</sup> INTERNATIONAL CONFERENCE ON CHEMICAL KINETICS

ORLÉANS, **JUNE 3 - 27 2019** 

COMBUSTION

CATALYSIS

**ATMOSPHERE** 



Depuis 80 ans, nos connaissances bâtissent de nouveaux mondes





UNIVERSITE D'ORLEANS Sc





	Monday, June 24	
08:00	Registration	
08:20	Welcome and Official Opening	
08:30-	Plen	ary 1
09:20		
	Is Gas Phase Chem	ical Kinetics Static?
	Kinetics in the Past, P	resent, and the Future
	A.R. Ravishankara, Color	ado State University, USA
	Chair: Georges Le Bras	
	Nove to par	allel sessions
	Session A1 (Ampni 2)	Session B1 (Ampni 3)
00.20	Chairs: C. Cavanolli/2. Serinyer	Chairs: G. Moorigal/B. Picquet-Variabilit
09.50	Complex Reacting Systems: Status Report	of the Old & CO & M & USO & M Pagetion
	W H Green	of the OH + SO <sub>2</sub> + IVI $\rightarrow$ HSO <sub>3</sub> + IVI Reaction
		M. McGillen, H Elothmani, Y. Ren, L. Zhou, M.
		Mellouki
09:50	Deep Learning of Activation Energies and	DMS H-Abstraction by OH in Excess in the
	Automated Reaction Dataset Generation	Absence of $O_2$
	C. Grambow, W.H. Green	Z. Salta, J. Lupi, O.N. Ventura, V. Barone
10:10	Automated Networks: Harnessing	Kinetic and Mechanistic Study of the
	Dynamics, Kinetics and Human Guided VR	Reaction CH <sub>3</sub> SO <sub>2</sub> NH <sub>2</sub> + OH
	for Blackbox Mechanism Generation	M. Berasategui, D. Amedro, A. Edtbauer, J.
	R.J. Shannon, D.V. Shalashilin, D.R. Glowacki	Williams, J. Crowley
10:30	Coffee	Break
11:00	Model Analysis Based Experimental	Employing pulsed irradiation in
	Design for Combustion Kinetics	photocatalysis
	B. Yang, J. Wang, Z. Zhou	T.P. Nicholls, J.C. Robertson, A.C. Bissember
11:25	Benchmarking DFT for Computational	Temperature and Pressure Dependence of
	Kinetics	the Kinetics of the CH <sub>2</sub> OO + CH <sub>3</sub> OO
	M.E. Segovia, O.N. Ventura, J. Lupi, Z. Salta, N.	Reaction
	Tasinato, V. Barone	R. Chhantyal Pun, N. Zachhuber, R. Martin,
		M.A.H. Knan, D.E. Snallcross, A.J. Urr-Ewing
11:45	Ketohydroperoxide Reactions Uncovered	Kinetic Studies of Self- and Cross-
11110	by KinBot	Reactions of Small Peroxy Radicals in the
	R. Van de Vijver, J. Zádor, G.B. Marin, K.M. Van	Highly Instrumented Reactor for
	Geem	Atmospheric Chemistry
		F.F. Østerstrøm, L. Onel, A. Brennan, J. Parr, E.
		Cooke, L. Whalley, P.W. Seakins, D.E. Heard

	Monday, June 24 (continued)	
12:05	Elementary-Reaction Kinetics for Cellulose and Hemicellulose Pyrolysis P.R. Westmoreland, A. Bose, C.J. McGill, A. Raghu	Development and Validation of a New Experimental Set-Up to Study Reactions Between Peroxy RO₂ and HOx Radicals F. Kravtchenko, L. Pillier, S. Batut, B. Calimet, C. Fittschen
12:25	Lunch	
	Session A2 (Amphi 2) Chairs: C.F. Goldsmith/P.A. Glaude	Session B2 (Amphi 3) Chairs: C. Fittschen/Y. Bedjanian
13:45	A Systematic Kinetic Modelling Study of Mono-Aromatic Hydrocarbons: Towards the Definition of Reaction Classes and Rate Rules M. Pelucchi, L. Pratali Maffei, R.D. Büettgen, W. Pejpichestakul, C. Cavallotti, A. Frassoldati, K.A. Heufer, T. Faravelli	Reactivity of OH Radicals Towards CH <sub>3</sub> CHO at T<200 K: Implications in Astrochemistry S. Blázquez, D. González, B. Ballesteros, A. Canosa, J. Albaladejo, E. Jiménez
14:05	Mechanistic Study of thermal degradation of β-1,4-D-xylan M. Goussougli, B. Sirjean, P.A. Glaude, R. Fournet	Pressure-Dependent Rate Constant Caused by Tunneling Effects: OH + HNO <sub>3</sub> as an Example T.L. Nguyen, J.F. Stanton
14:25	An Experimental and Chemical Kinetic Modeling Study of 1,3-Butadiene Combustion: Ignition Delay Time and Laminar Flame Speed Measurements C.W. Zhou, Y. Li, U. Burke, C. Banyon, K.P. Somers, S. Ding, S. Khan, J.W. Hargis, T. Sikes, O. Mathieu, E.L. Petersen, M. AlAbbad, A. Farooq, Y. Pan, Y. Zhang, Z. Huang, J. Lopez, Z. Loparo, S.S. Vasu, H.J. Curran	Reaction Between Peroxy and Alkoxy Radicals Can Form Stable Adducts M. Rissanen, S. Iyer, T. Kurtén
14:45	Group Additive Kinetic Modeling for the Pyrolysis of Cyclic Species F.H. Vermeire, R. Van de Vijver, G.B. Marin, K.M. Van Geem	Pressure Dependent Kinetics of the Reaction Between CH <sub>3</sub> O <sub>2</sub> and OH: Triox Formation C. Yan, L.N. Krasnoperov
15:05	The Criegee Intermediate Reaction Network in Ethylene Ozonolysis N. Hansen, A.C. Rousso, A.W. Jasper, Y. Ju	Pressure-Dependent Kinetics of the Reaction Between CH <sub>3</sub> O <sub>2</sub> and OH Focusing on the Product Yield of Methyltrioxide (CH <sub>3</sub> OOOH) <i>F. Zhang, C. Huang</i>
15:30	Coffee Break	

	Monday, June 24 (continued)		
16:00	Modeling PAH Formation using RMG: From Acetylene to Three Rings M. Liu, T.C. Chu, A. Jocher, M.C. Smith, W.H. Green	Reaction Products of Fuel Derived CH Radical Reactions with Ammonia and Substituted Amines by Using SVUV Photoionization Coupled to Time-of-Flight Mass Spectrometry J. Bourgalais, K. Caster, O. Durif, D. Osborn, S. Le Picard, F. Goulay	
16:20	Direct Measurements of PAH Formation and Growth by Addition of Phenyl and Naphthyl Radicals to Acetylene M.C. Smith, T.C. Chu, J. Yang, A. Uwagwu, M. Liu, W.H. Green	<b>Reaction OH + OH</b> $\rightarrow$ H <sub>2</sub> O + O Revisited X. Zhang, M. Sangwan, C. Yan, P.V. Koshlyakov, E.N. Chesnokov, L.N. Krasnoperov	
16:40	Move to ple	nary session	
16:50- 17:40	Plenary 2 Quantum Chemical Modeling of Mechanisms and Selectivities in Homogeneous Catalysis F. Himo, Stockholm University Chair: Vicent Moliner		
19:00	Recention at	Hôtel Groslat	
20:00	End of Day		

	Tuesday, June 25		
08:00	Registration		
08:20	Daily announcements		
08:30-	Plen	ary 3	
09:20	Chamical Kinatics of Multin	haca Atmacabaric Chamistry	
		India El Iniversity 1154	
	V. Faye Michelli, Columbia University, USA		
	Chair: Hartm	nut Herrmann	
	Move to parallel sessions		
	Session A3 (Amphi 2)	Session B3 (Amphi 3)	
	Chairs: K. Brezinsky/A. Farooq	Chairs: J. Chen/I. Bejan	
09:30	Reactivity Comparison of Linear C4-C6	A Gas-phase Reaction Model for Si-CVD	
	Alcohol, Aldehyde and Carboxylic Acid	Simulation under Atmospheric or	
	Oxidation	Moderate Pressure	
	S. Namysi, M. Pelucchi, O. Herbinet, T. Faravelli,	K. Noda, N. Kunioshi, Y. Jagawa, A. Fuwa	
09:50	Detailed Experimental and Kinetic	Coupling Between Gas-Phase and Surface	
	Modeling Study of 3-Carene Pyrolysis	Chemistry in Catalytic Combustion	
	J. Zhang, F.H. Vermeire, R. Van de Vijver, O.	K. Blondal, J. Jelic, E. Mazeau, F. Studt, R.H.	
	Herbinet, F. Battin-Leclerc, M.F. Reyniers, K.M.	West, C.F. Goldsmith	
	Van Geem		
10:10	A Theoretical and Kinetic Analysis of	π-Hydrogen Bonding Probes Chemical	
10110	Phenol Pyrolysis	Reactivity: Bromination of C=C Double	
	L. Pratali Maffei, M. Pelucchi, T. Faravelli, C.	Bond, Electrophilic Aromatic Nitration and	
	Cavallotti	Benzylation	
		B. Galabov, G. Koleva, B. Hadjieva, H. F.	
		Schaefer III	
10:30	Coffee Break		
11:00	Ignition Phenomena in Diethyl Ether/Air	Biomass-Burning Related Atmospheric	
	Mixtures: Elementary Steps, Mechanism,	Aqueous-Phase Chemistry: Kinetics,	
	and Transport	Photochemistry and Modelling	
	J. Eble, J. Kiecherer, C. Bänsch, M. Olzmann	H. Herrmann, T. Scahefer, L. He, T. Felber, A.	
		Tilgner, E.H. Hoffmann	
11:25	Effect of Methyl Group Substitution on	Effect of Surface/Bulk Partitioning on the	
11120	the Kinetics of Vinyl Radical Oxidation	Heterogeneous Kinetics of Aqueous	
	S.P. Joshi, T.T. Pekkanen, R.S. Timonen, A.J.	Droplets	
	Eskola	F. Goulay, H Fan, T.W. Massaya	
11:45	Kinetics of the Competing C-O Bond-	Atmospheric Chemistry of lodous and	
	Fission Reactions of Dimethoxymethane	IOGIC ACIOS	
	L. GOIKU, D. GLULZJEIU, I. WEDEL, IVI. OIZITIUTIN	M. Ribaucour, I. Cernusak, I. Cantrel F Louis	

	Tuesday, June	25 (continued)
12:05	High-Temperature Shock Tube Ignition Study of Prenol Isomers E. Ninnemann, A. Laich, S. Neupane, K. Thurmond, S. Vasu	Shielding of Aerosol-Borne Pesticides Against OH Radicals L. Han, C. Zetzsch
12:25	Lunch	
	<b>Session A4 (Amphi 2)</b> Chairs: M. Olzmann/R. Fournet	Session B4 (Amphi 3) Chairs: K. Noda/V. Belandria
13:45	Ignition Delay Times of Dibutylether in a Rapid Compression Machine F. Khaled, Z. Serinyel, G. Dayma, F. Foucher	Polymer Mixtures Thermal Degradation Kinetic Analysis J. Briceno, M.A.N.D.A. Lemos, F. Lemos
14:05	<b>CO Formation from Dimethyl-Carbonate</b> <b>Pyrolysis Behind Reflected Shock Waves</b> <i>O. Mathieu, C.R. Mulvihill, E.L. Petersen</i>	Theoretical and Experimental Studies of the Thermal Oxidation of Epoxy-Amine Systems R. Delannoy, E. Richaud, V. Tognetti
14:25	<b>Shock Tube Study of the Pyrolysis Kinetics</b> <b>of Di- and Trimethoxy Methane</b> <i>M. Döntgen, M.E. Fuller, C.F. Goldsmith</i>	Thermal and Catalytic Degradation of Polypropylene with VGO and UCO T. Godinho, M.A.N.D.A. Lemos, H. Carabineiro, L. Tarelho, F. Lemos
14:45	Oxidation of an Iso-Paraffinic Alcohol-to- Jet Fuel and Heptane Mixture: An Experimental and Modelling Study J. Guzman, G. Kukkadapu, K. Brezinsky, C. Westbrook	Fundamentals of Polymer Fouling in Ethylene Crackers M. Forsuelo, D. Ranasinghe, H.W. Pang, L. Lai, M.C. Smith, M. Goldman, W.H. Green
15:05	Reaction Kinetics of Hydroxyl Radicals with Dienes A. Farooq, B. Giri	Revealing the Origin of the Catalytic Power of Enzymes by Merging Computational Studies and Experiments S. Martí, R. Castillo, K. Świderek, M. Roca, K. Arafet, D. De raffele, N. Serrano, M.A. Galmes, V. Moliner
15:30	Coffee	Break
16:00	Shock-Tube Measurements of CO Concentration Time-Histories During Iso- Octane Oxidation O. Mathieu, S. Cooper, S. Alturaifi, C.R. Mulvihill, E.L. Petersen	TG/DSC Analysis of the Pyrolysis Kinetics of Polystyrene from WEEE R. Kol de Carvalho, B. Rijo, F. Rey, T. Carvalho, F. Lemos, M.A.N.D.A. Lemos

	Tuesday, June 25 (continued)	
16:20	Dual-Comb Spectroscopy in Shock Tubes:	Catalytic Pyrolysis Kinetics of Polystyrene
	Mid-Infrared Microsecond-Resolved	from WEEE
	Spectrometer	P. Pereira, F. Rey, B. Rijo, T. Carvalho, F. Lemos,
	A. Hugi, M. Geiser, R. Horvath, C.I. Strand, N.	M.A.N.D.A. Lemos
	Pinkowski, Y. Ding, R.K. Hanson	
16:40	Experimental and Kinetic Modeling	Formation Kinetics of Water-Soluble
	Investigation on Laminar Flame	Lanthanide(III) Porphyrins as Potential
	Propagation of Engine Fuels in a High-	Biomedical Agents
	Pressure Constant-Volume Cylindrical	Z. Valicsek, M.P. Kiss, O. Horváth
	Combustion Vessel	
	Y. Li, B. Mei, X. Zhang, W. Li, S. Ma, G. Wang,	
	W. Yuan	
17:00	Laminar Burning Velocities and LIF	Chemistry Triggered Events of PM2.5
	Measurements of Nitric Oxide Formation	Explosive Growth During Late Autumn and
	in Flames of Simple Alcohols	Winter in a Megacity
	C. Brackmann, T. Methling, G. Capriolo, M.	W. Sun, D. Wang, L. Yao, Q. Fu, H. Wang, Q. Li,
	Lubrano Lavadera, A.A. Konnov	G. Wange, J. Chen
17:25	Move to ple	nary session
17:35-	Plen	ary 4
18.25		
10.25	High-Temperature	Reaction Pathways
	T. Kasper, Duisburg-Ess	en University. Germany
	Chair: Philip R. Westmoreland	
18:30	Poster Session and Cocktail	
22:00	End of Day	

	Wednesday, June 26	
08:00	Registration	
08:20	Daily announcements	
08:30-	Plen	ary 5
09:20		
	Theoretical Studies of the Atmosphe	ric Chemical Mechanisms of Isoprene
	and its Oxida	tion Products
	G. Da Silva, University o	of Melbourne, Australia
	Chair: Willio	am H. Green
	Move to par	allel sessions
	Session A5 (Amphi 2)	Session B5 (Amphi 3)
	Chairs: K. Van Geem/F. Zhang	Chairs: O. Mathieu/A. Frassoldati
09:30	A Kinetic View on Dissociative Electron	Rate Constant Measurements and RRKM
	Attachment Processes	Modeling on Thermal Decomposition of
	J. Troe, A.A. Viggiano	Ethylsilanes and Cyclosiloxanes
		S. Peukert, P. Sela, Y. Sakai, J. Herzler, M. Fikri,
		C. Schulz
09.20	Understanding Temperature and Pressure	Impact of Correlated Inputs on Computed
05.50	Dependence in the Non-Adiabatic	Branching Ratio
	Reactions of Oxygen Atoms with Terminal	C. Huana, Z. Zhou, B. Yana, F. Zhana
	Alkenes	5, , 5, 5
	C. Cavallotti, L. Pratali Maffei, A. Caracciolo, N.	
	Balucani, P. Casavecchia	
10:10	New Phenomenological Reaction Rate	Determination of Bond Additivity
	Equation for Chemical Catalyst	Corrections for CBS-QB3 Calculated
	Deactivation (Reversible-Irreversible Case)	Standard Enthalpies of Formation of C, H,
	Z.J.G. Gromotka, G.S. Yablonsky, G.B. Marin, D.	N, O and S species
	Constales	C.A.R. Pappijn, R. Van de Vijver, F.H. Vermeire,
		M.F. Reyniers, G.B. Marin, K.M. Van Geem
10.30	Coffee	Break
11:00	Electrode Kinetics of Strongly Adsorbed	On the Combustion Chemistry of Alkyl
	Molecules on Semiconductors: Isolating	Nitrates
	Kinetic Constants from Lateral	C.F. Goldsmith, M.E. Fuller, N. Chaumeix
	Interactions and Diode Parameters	
	S. Ciampi, Y.B. Vogel, A. Molina	
11:25	Comparative Methods of Kinetic Analysis	Pyrolysis Mechanism and Kinetics of
	of Calcium Looping for Energy Storage	Isopropyl Nitrate
	L. Fedunik-Hofman, A. Bayon, W., Lipiński, S.W.	M.E. Fuller, C.F. Goldsmith
	Donne	

	Wednesday, June 26 (continued)		
11:45	First-Principles Calculation of Catalytic Activity Modifications with an Electric Field K. Wakamatsu, T. Ogura	Shock Wave and Modelling Study of the Dissociation Pathways of (C <sub>2</sub> F <sub>5</sub> ) <sub>3</sub> N E. Tellbach, C.J. Cobos, L. Sölter, J. Troe	
12:05	Theoretical Kinetic Study of Formic Acid Catalyzed Keto-Enol Tautomerizations for C <sub>2</sub> And C <sub>3</sub> Enols at Conditions Relevant to Atmospheric and Combustion Chemistry E. Grajales-González, M. Monge-Palacios, S.M. Sarathy	<b>Reaction Pathways of Cyclopentanone</b> <b>Oxidation Intermediates</b> <i>S. Khanniche, W.H. Green</i>	
12:25	How Can Cells Detect and Respond to Oxygen Levels? Computer Simulations Studies of Oxygen Diffusion into Prolyl Hydroxylases C. Domene	The Pyrolysis Chemistry of Propionic Acid and Ethyl Propionate Revealed C. Rogers, K. Cummins, J. Porterfield, J.W. Daily, G.B. Ellison, N.J. Labbe	
12:50	Lunch Boxes		
14:00	Bus departure to the "Château de Chambord"		
15:30	Free time and visit		
18:30	Cocktail on	the Terraces	
20:00	Banquet on the 1 <sup>st</sup> floor around the double helix staircase		
23:00	End of Day		

	Thursday, June 27	
08:00	Registration	
08:20	Daily announcements	
08:30-	Plenary 6	
09:20	Poactivity of Biogonic Volatilo Org	anic Compounds with NOs Padical
	B Picquet-Varrault Unive	aric Compounds with No3 Naulcal
	Chair: Gil	les Poulet
	Move to par	allel sessions
	Session A6 (Amphi 2)	Session B6 (Amphi 3)
	Chairs: A. Konnov/N. Hansen	Chairs: E. Jiménez/M. McGillen
09:30	Thermal Decomposition of Spray in Plug-	Gas-Phase Rate Coefficients for the
	Flow Reactor at Atmospheric Pressure	Reaction of the NO <sub>3</sub> Radical with a Series
	M. Gonchikzhapov, T. Kasper	of Aromatic Aldehydes
		Y. Ren, M. McGillen, A.R. Ravishankara, S.S.
		Brown, L. Zhou, M. Idir, V. Daële, A. Mellouki
09:50	Preliminary Results on Syngas Kinetic	Atmospheric Oxidation Mechanism of
	Mechanism Optimization Using the New	Toluene Initiated by OH Radical
	Opt-D* Algorithm	X. Wu, C. Huang, F. Zhang
	S.M. Ali, S. Varunkumar	
10:10	Instabilities of H <sub>2</sub> -O <sub>2</sub> System and Effect of	Water Vapor Does Not Catalyze the
	Several Bath Gases	Reaction Between Methanol and OH
	P. Sabia, M.V. Manna, M. de Joannon, R.	Radicals
	huguet	C. Schoemdecker, W. Chuo, J.Jr.M. Lin, K. Takahashi A Tomas I Yu Y Kajij S Batut C
		Fittschen
10:30	Coffee	Break
11:00	Fast Pyrolysis Bio-Oil Combustion	Photosensitization in the Air: Bridging
	Characteristics and Challenges for Kinetic	Fundamental Bulk Processes with
	Modeling	Secondary Organic Aerosol Production
	A. Frassoldati, M. Pelucchi, A.E. Saufi, A. Cuoci,	C. George
	C. Cavanotti, T. Furaveni, E. Ranzi	
11:25	Experimental and Kinetic Study of 1,2,4-	Anthraguinone-2-Sulfonate as a Model for
	Trimethylcyclohexane Pyrolysis	Photoinduced Reactions in Tropospheric
	Y.X. Liu, D.X. Tian, C.C. Cao, Z.K. Liu, Y.T. Zhai, Y.	Aqueous Aerosol
	Zhang, J.Z. Yang, Z.Y. Tian	T. Schaefer, J.D. Raff, H. Herrmann
11.45	A Comprehensive Experimental and	Development and Validation of a Teflor
11.45	Kinetic Modeling Study of o-Xylene	Thermal Regulated Atmospheric
	Combustion	Simulation Chamber (THALAMOS), A
	W. Yuan, I. Zhao, W. Li, Y. Li, P. Dagaut, F. Oi, J.	Versatile Tool for the Study of
	Yang	Atmospheric Relevant Processes
		N. Osseiran, M.N. Romanias, V. Gaudion, M.
		Angelaki, V.C. Papadimitriou, A. Tomas, F.
		Thevenet, P. Coddeville

	Thursday, June 27 (continued)	
12:05	High-Temperature Fast-Flow Reactor for the study of Radical-Radical Reactions Y. Lee, F. Goulay	Atmospheric Reactivity of Biogenic Volatile Organic Compounds under the Canopy of a Maritime Pine Forest during the LANDEX Field Campaign K. Mermet, S. Sauvage, S. Dusanter, T. Salameh, T. Léonardis, N. Locoge, P.M. Flaud, E. Perraudin, E. Villenave
	Structure of a Counterflow Flame at Different Operating Conditions S.A. Gómez, V. Zhukov, C.R. de Andrade, A.P. Pimenta	First-Principles Kinetic Monte Carlo Study of Hydrodeoxygenation at the Ru/TiO <sub>2</sub> Interface X. Li, L.C. Grabow
12:25	Lunch	
	Close of conference	

## **TUESDAY EVENING POSTER SESSION PROGRAM**

#### Poster #1

#### CHAMBER STUDY OF THE OXALYL CHLORIDE PHOTODISSOCIATION IN SUNLIGHT

Kukui Alexandre, Ren Yangang, Daële Véronique, Mellouki Wahid, Ravishankara A. R.

#### Poster #2

## A NEW KINETICS DATABASE OF ORGANIC OXIDATION REACTIONS FOR USE IN STRUCTURE-ACTIVITY RELATIONSHIP STUDIES

McGillen Max, Orlando John, Mellouki Abdelwahid, Picquet-Varrault Bénédicte, Wallington Timothy, Carter William

#### Poster #3

## **EFFECTS OF THE AXIAL LIGANDS ON THE FORMATION KINETICS OF WATER-SOLUBLE CERIUM(III) PORPHYRINS** Valicsek Zsolt, Kiss Melitta, Horvath Otto

#### Poster #4

## GAS PHASE KINETIC STUDY FOR A SERIES OF METHYLATED FURANS WITH CHLORINE ATOMS IN ATMOSPHERIC CONDITIONS Claudiu Roman, Arsene Cecilia, Olariu Romeo, Bejan Iustinian

### Poster #5

### GAS PHASE KINETIC STUDY FOR A SERIES OF METHYLATED AROMATICS WITH OH RADICALS

Bejan Iustinian, Gibilisco Rodrigo, Barnes Ian, Wiesen Peter

#### Poster #6

TROPOSPHERIC DEGRADATION OF BIOMASS BURNING COMPOUNDS: OH RADICAL-INITIATED OXIDATION OF THREE DIMETHOXYBENZENE ISOMERS AND 4-VINYLGUAIACOL.

*Gibilisco Rodrigo, Barnes Ian, Bejan Iustinian, Wiesen Peter* 

### Poster #7

GAS PHASE KINETIC AND THEORETICAL APPROACH ON THE CHLORINE ATOM CHEMISTRY OF EPOXIDES

Tovar Carmen, Haack Alexander, Barnes Ian, Bejan Iustinian, Wiesen Peter

### Poster #8

## IUPAC TASK GROUP ON ATMOSPHERIC CHEMICAL KINETIC DATA EVALUATION

Ammann M., Cox R., Crowley J., Herrmann J., Jenkin M., McNeill V., Mellouki A., Troe J., Wallington T.

#### Poster #9 **KINETIC ANALYSIS OF GROWTH MECHANISM OF PAHS THROUGH C5 RINGS** *Pejpichestakul Warumporn, Pelucchi Matteo, Cavallotti Carlo, Frassoldati Alessio, Faravelli Tiziano*

Poster #10

## TOWARDS A COMMON CO-C2 MECHANISM: A CRITICAL EVALUATION OF RATE CONSTANTS FOR HYDROGEN COMBUSTION KINETICS.

Pelucchi Matteo, Burke Ultan, Cai Liming, Somers Kieran, Glarborg Peter, Turanyi Tamas, Heinz Pitsch, Curran Henry, Faravelli Tiziano, Stephen Klippenstein

Poster #11

## REACTION GENERALIZATION OF SINGULAR SITE USING LOCAL SURFACE MODEL

Takata Yasumasa, Ogura Teppei

Poster #12

## EXAMINATION OF AUTOMATIC GENERATION ALGORITHM OF CATALYST SURFACE REACTION MECHANISM

Aratani Masato, Ogura Teppei

## Poster #13

## PRELIMINARY RESULTS ON TRACING AIR POLLUTION AND IMPACT ON OZONE IN DIFFERENT PLUMES USING AIRCRAFT MEASUREMENTS IN DACCIWA EUROPEAN PROJECT

Xue Chaoyang, Krysztofiak Gisèle, Brocchi Vanessa, Stratmann Greta, Sauer Danie, Schlager Hans, Lee James, Hopkins James, Colomb Aurélie, Borbon Agnès, Catoire Valéry

Poster #14 KINETICS OF THE GAS PHASE REACTION BETWEEN THE CRIEGEE INTERMEDIATE CH2OO AND O3 Onel Lavinia, Blitz Mark, Seakins Paul, Heard Dwayne, Stone Daniel

Poster #15 DIRECT MEASUREMENTS OF THE KINETICS OF THE REACTION BETWEEN THE CRIEGEE INTERMEDIATE CH3CHOO AND SO2 Onel Lavinia, Mortiboy Jennifer, Blitz Mark, Seakins Paul, Heard Dwayne, Stone Daniel

Poster #16

**UNIMOLECULAR DECOMPOSITION OF THE ALLYLIC METHYL CROTONATE RADICAL: EXPERIMENTAL AND MODELLING STUDY** Seal Prasenjit, Joshi Satya, Eskola Arkke Poster #17

GAS-PHASE POSITIVE ION INSIGHTS DURING LABORATORY EUV IRRADIATION OF N2/CH4 GAS MIXTURES: IMPLICATIONS FOR TITAN'S IONOSPHERIC CHEMISTRY

Bourgalais Jérémy, Pernot Pascal, Carrasco Nathalie

Poster #18

FIRST PEPICO SPECTROSCOPY INVESTIGATIONS OF N-PENTANE LOW TEMPERATURE OXIDATION IN A JET-STIRRED REACTOR

Bourgalais Jérémy, Battin-Leclerc Frédérique, Herbinet Olivier, Wang Zhandong, Tran Luc-Sy, Vanhove Guillaume, Nahon Laurent, Garcia Gustavo

Poster #19

PHOTODEGRADATION OF A SERIES OF FLUOROESTERS INITIATED BY OH RADICALS AT DIFFERENT TEMPERATURES

Lugo P., Rivella C., Gibilisco Rodrigo, Salgado S., Wiesen Peter, Blanco M. B., Teruel Mariano

Poster #20

GAS-PHASE DEGRADATION OF 2-BUTANETHIOL INITIATED BY CL ATOMS. KINETICS, PRODUCT YIELDS AND MECHANISM AT 298K AND ATMOSPHERIC PRESSURE

L. Cardona Alejandro, Gibilisco Rodrigo, Wiesen Peter, Teruel Mariano

Poster #21

SHOCK WAVE AND THEORETICAL MODELING STUDY OF THE DISSOCIATION OF CH2F2 - PRIMARY AND SECONDARY REACTIONS

Soelter Lars, Tellbach Elsa, Cobos Carlos, Troe Jurgen

Poster #22

PREMIXED FLAME STRUCTURE OF ETHYL PENTANOATE: EXPERIMENTAL STUDY AND CHEMICAL KINETIC MODELING

Dmitriev Artem, Osipova Ksenia, Bolshova Tatiana, Knyazkov Denis, Glaude Pierre-Alexandre

Poster #23 KINETICS AND MECHANISM OF BrHgO WITH CO Khiri Dorra, Dibble Theodore, Cernusak Ivan, Louis Florent

KIIII Dolla, Dibble Theodole, Certusak Ivali, Louis P

Poster #24
THEORETICAL INVESTIGATION OF THE REACTION CI + HOIO

Suliman Siba, Taamalli Sonia, Khiri Dorra, Cernusak Ivan, Cantrel Laurent, Louis Florent

Poster #25

A THEORETICAL STUDY OF PYRENE FORMATION FROM FLUORANTHENE

Khiri Dorra, Dao Duy Quang, Nguyen Thanh Binh, Gasnot Laurent, Louis Florent, El Bakali Abderrahman

Poster #26

REACTIVITY OF NO3 RADICAL WITH MONOTERPENES: THEORETICAL APPROACH FOR MECHANISTIC STUDY

Rayez Marie-Thérèse, Cirtog Manuela, Rayez Jean-Claude, Picquet-Varrault Bénédicte, Fouqueau Axel

Poster #27

**DEVELOPMENT OF A STAGNATION PLATE BURNER AS A NEW SUPPORT TO STUDY COOL FLAME CHEMISTRY** *Mokrani Nabil, Panaget Thomas, Batut Sébastien, Pillier Laure, Vanhove Guillaume* 

Poster #28

## ROOOH: A SOURCE OF INTERFERENCE FOR OH MEASUREMENTS IN LOW NO ENVIRONMENTS

Fittschen Christa, Al Ajami Mohamad, Batut Sebastien, Ferracci Valerio, Archer-Nicholls Scott, Archibald Alexander T., Schoemaecker Coralie

Poster #29

INCOHERENT BROAD-BAND CAVITY ENHANCED ABSORPTION SPECTROSCOPY FOR SENSITIVE AND RAPID MOLECULAR IODINE DETECTION IN THE PRESENCE OF AEROSOLS AND WATER VAPOUR

Bahrini Chiheb, Grégoire Anne-Cécile, Obada Dorel, Mun Christian, Fittschen Christa

Poster #30 EXPERIMENTAL AND THEORETICAL DETERMINATION OF DMC/AIR FLAME VELOCITIES

De Persis Stephanie, Chaumeix Nabiha, Fernandes Yann, Bry Alain, Comandini Andrea

Poster #31 LAMINAR BURNING VELOCITY OF BIOGAS AND SYNGAS FLAMES Boushaki Toufik, Zaidaoui Hajar

#### Poster #32

**OXIDATION OF METHYL-SUBSTITUTED BENZENES: EXPERIMENTAL AND THEORETICAL INVESTIGATIONS OF INITIATION REACTIONS** *Kounlavong Sommy, Izumi Naoto, Sasaki Yu, Oguchi Tatsuo* 

Poster #33

**FORMALDEHYDE FROM A CHEMICAL SOURCE FOR DETECTION AND CALIBRATION WITH LASER-INDUCED FLUORESCENCE** *Kuehn Christian, Olzmann Matthias* 

Poster #34

**QUANTUM CHEMICAL STUDY OF DECOMPOSITION AND CONDENSATION REACTIONS OF UREA** *Gratzfeld Dennis, Olzmann Matthias* 

Poster #35

MASS SPECTROMETRIC STUDY OF PROCESSES OF HALOGEN-CONTAINING ACIDS IN GAS AND WATER Morozov Igor

Poster #36

**HIGHLY OXYGENATES MOLECULES FORMED BY OXIDATION OF TERPENES IN A JET-STIRRED REACTOR** *Dagaut Philippe, Belhadj Nesrine, Benoit Roland, Dayma Guillaume, Lailliau Maxence, Serinyel Zeynep* 

Poster #37

**GAS-PHASE KINETICS AND PRODUCT STUDY OF THE CL REACTION WITH TRANS-2-METHYL-2-BUTENAL** *Garcia-Saez Alberto, Antinolo Maria, Asensio Maria, Albaladejo José, Jiménez Elena* 

Poster #38

KINETICS OF OH RADICALS WITH HNO3 BETWEEN 21.7 K AND 177.5 K IN THE GAS PHASE Jiménez Elena, Gonzalez Daniel, Blazquez Sergio, Ravishankara A. R.

Poster #39

LOW PRESSURE REACTION KINETICS OF OH+HNO3 IN AN EXTENDED TEMPERATURE RANGE Bedjanian Yuri, Ravishankara A. R. Poster #40 THEORETICAL STUDY ON THE HYDROGEN ABSTRACTION REACTIONS FROM HYDRAZINE DERIVATIVES BY H ATOM Kanno Nozomu, Kito Tomohiro

#### Poster #41

**CALCULATION OF THE ABSOLUTE PHOTOIONIZATION CROSS-SECTIONS FOR C1-C4 CRIEGEE INTERMEDIATES AND VINYL HYDROPEROXIDES** *Huang Can, Yang Bin, Zhang Feng* 

Poster #42 ORGANO-PHOSPHOROUS FIRE SUPPRESSANTS AND THEIR REACTIONS WITH H ATOMS Dievart Pascal, Catoire Laurent

Poster #43 **ATMOSPHERIC DEGRADATION OF 3-ETHOXY-1-PROPANOL**  *Aranda Maria Inmaculada, Martin Pilar, Salgado Sagrario, Cabañas Beatriz* Poster #44 **KINETIC DISSOLUTION, VALIDATION, STATISTICAL MODELS OF A NEW GENERIC TABLETS OF LORATADINE** 

Guermouche Saliha

# **PLENARY LECTURES**

## Is Gas Phase Chemical Kinetics Static? Kinetics in the past, present, and the future

A.R. (Ravi) Ravishankara<sup>1,2,3</sup>

<sup>1</sup>Departments of Chemistry and Atmospheric Science, Colorado State University, Fort Collins, CO 80235, US <sup>2</sup>Le Studium Institute for Advances Studies, Orléans, FRANCE <sup>3</sup>CNRS-INSIS, Institut de Combustion, Aérothermique, Réactivité et Environnement, 1C Avenue de la recherche scientifique, 45071 Orléans cedex 2, FRANCE

Keywords

Chemical kinetics, Gas phase

Even though the field of gas phase chemical kinetics started as a curiosity driven science attempting to measure and understand rates of chemical reactions, in the 20<sup>th</sup> century it took on a decidedly useinspired research flavor. The main uses were to improve combustion processes and understand atmospheric environmental issues, along with applications in varied fields such as astrochemistry. It encompassed understanding mechanisms of chemical reactions, determining the speed of reactions, and prediction of energy release, end-products, intermediates, and loss processes. These studies have been critical for advances in combustion and atmospheric chemistry, with major successes.

I will look back at the past learning experiences, assess the present status (decidedly subjective!), and guess at where this field is needed and likely to go in the future.

Examples will be taken from work that I am associated with as well as from others.

\*Corresponding author: a.r.ravishankara@colostate.edu

## Quantum Chemical Modeling of Mechanisms and Selectivities in Homogeneous Catalysis

## Fahmi Himo

Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University, SE-10691 Stockholm, Sweden. fahmi.himo@su.se

Using modern density functional theory methods it is today possible to routinely and accurately treat relatively large systems. The calculated energies can be used to rule out or substantiate reaction mechanisms and have also been shown to be sufficiently accurate to satisfactorily reproduce various kinds of selectivities. These developments have made it possible to tackle increasingly difficult problems in homogeneous catalysis.

This talk will give a brief account of the methods used and discuss some recent results in this field, in which we take advantage of both DFT calculations and kinetics simulations to understand reaction mechanisms and rationalize the origins of selectivities.[1-3]

[1] Stefano Santoro, Marcin Kalek, Genping Huang, Fahmi Himo,

Elucidation of Mechanisms and Selectivities of Metal-Catalyzed Reactions using Quantum Chemical Methodology,

Acc. Chem. Res. 2016, 49, 1006–1018.

[2] Marcin Kalek, Fahmi Himo,

Mechanism and Selectivity of Cooperatively-Catalyzed Meyer-Schuster Rearrangement/Tsuji-Trost Allylic Substitution. Evaluation of Synergistic Catalysis by Means of Combined DFT and Kinetics Simulations,

J. Am. Chem. Soc. 2017, 139, 10250–10266.

[2] Henrik Daver, Jeremy N. Harvey, Julius Rebek Jr., Fahmi Himo,

Quantum Chemical Modeling of Cycloaddition Reaction in a Self-Assembled Capsule,

J. Am. Chem. Soc. 2017, 139, 15494–15503.

## CHEMICAL KINETICS OF MULTIPHASE ATMOSPHERIC CHEMISTRY

V. Faye McNeill<sup>1,\*</sup>

<sup>1</sup>Department of Chemical Engineering, Columbia University, New York, NY 10025 USA

Keywords

aqueous chemistry, clouds, aerosols, atmospheric chemistry, chemical kinetics

Multiphase chemistry in the atmosphere is a major source of organic and inorganic atmospheric particulate matter, and also has a profound influence on gas-phase composition and precipitation chemistry. Despite considerable progress, mechanistic understanding of some key aqueous atmospheric processes is still lacking, and their representation is incomplete in most regional and global models. I will present an overview of aqueous chemical processes in the atmosphere, highlighting recent developments and critical uncertainties. I will also discuss my group's efforts in characterizing these processes in the laboratory and improving their representation in atmospheric chemistry models.

## **HIGH-TEMPERATURE REACTION PATHWAYS**

Tina Kasper<sup>1\*</sup>, Martin Höner<sup>1</sup>, Dennis Kaczmarek<sup>1</sup>, Yasin Karakaya<sup>1</sup>, Munko Gonchikzhapov<sup>1</sup>, Sebastian Peukert<sup>2</sup>, Dominik Krüger<sup>3</sup>, Thomas Bierkandt<sup>3</sup>, Markus Köhler<sup>3</sup>, Patrick Hemberger<sup>4</sup>

<sup>1</sup>Mass Spectrometry in reactive flows, IVG, University of Duisburg-Essen, Lotharstr. 1, 47057 Duisburg, Germany

<sup>2</sup>Reactive Fluids, IVG, University of Duisburg-Essen, Lotharstr. 1, 47057 Duisburg, Germany
 <sup>3</sup>German Aerospace Center – Institute of Combustion Technology, Stuttgart 70569, Germany
 <sup>4</sup>Laboratory for Femtochemistry and Synchrotron Radiation, Paul Scherrer Institute, Switzerland

Keywords

Combustion, PEPICO, Molecular-beam mass spectrometry

Despite considerable efforts towards electrification of the transport and residential sectors, combustion remains the major energy conversion process in almost all mid-term energy scenarios and is an integral part of several industrial production processes. Chemical kinetic knowledge is required to adjust to new fuels and anticipate their emissions, control auto ignition, develop power-to-chemicals concepts, or understand the reaction pathways that lead to the formation of functional materials in flame synthesis.

The first step in the development of reaction schemes is to identify the species involved in the reaction network. Photo electron photoion coincidence (PEPICO) spectroscopy in combination with molecular-beam sampling is an excellent tool for this purpose because of the high sensitivity towards radicals, and a superior identification of isomeric species.

The flame-sampling PEPICO setup was used to investigate the abstraction of chemically different hydrogen atoms from several hydrocarbon fuels in low-pressure hydrogen flames doped with different alkanes and alkenes. A detailed knowledge of important reaction steps during combustion of aromatics is also required for emissions control. Two reaction routes are of interest for pollutant formation in toluene combustion: the oxidation of toluene and the formation of larger polycyclic aromatic hydrocarbons (PAH). Key intermediates of toluene oxidation were detected, e.g. benzyl radicals and  $C_5H_5CCH$ . It was observed that most PAH are not formed from the aromatic fuel, but from small radicals such as propargyl and allyl.

Beside investigations of laminar flame chemistry, initial results from recently commissioned reactor experiments, including a jet-stirred reactor and a high pressure plug-flow reactor, obtained with the PEPICO spectrometer at the Swiss Light Source will be presented.

The flame conditions and the interaction of the precursor molecules with flame species determine the formation pathways of larger molecules in flame synthesis processes, in homogenous gas flames and spray flames. Based on the experimentally observed intermediates formed in the flame synthesis of silica particles from tetramethylsilane, a reaction sequence that leads to cluster and particle formation is suggested. Also, initial measurements for the elucidation of reaction pathways in spray flame are shown.

PEPICO and molecular-beam mass spectrometry allow the detection of stable, radical and ionic flame species without prior knowledge of their molecular properties, have a large dynamic range, and typically high sensitivity, but they require extraction of a sample from the reacting system. The introduction of a sampling probe influences the system temperature and can change species concentrations. Examples of these effects are discussed.

\*Corresponding author: tina.kasper@uni-due.de

## Theoretical Studies of the Atmospheric Chemical Mechanisms of Isoprene and its Oxidation Products

Gabriel da Silva<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, The University of Melbourne, Victoria 3010, AUSTRALIA

Keywords

Isoprene, oxidation, theoretical calculations.

Isoprene is one of the most emitted compounds to Earth's atmosphere, and largely controls chemical composition in remote, forested environments. Despite the importance of isoprene in atmospheric science, the chemistry of many of its key chemical degradation pathways are not yet fully understood. This talk will highlight our recent theoretical studies on new atmospheric reaction pathways of isoprene and its oxidation products.

In the troposphere isoprene reacts rapidly with OH and then  $O_2$  to produce a suite of hydroxyperoxyl radicals (ISOPO<sub>2</sub>), incorporating  $\beta$ -OH and E/Z  $\delta$ -OH functionality. It has been shown that the  $\delta$ -(Z)-ISOPO<sub>2</sub> radicals can undergo a facile intramolecular hydrogen shift to produce a 1-hydroxyalkyl radical intermediate which can react with O<sub>2</sub> to yield a HPALD. This work shows that these ISOPO<sub>2</sub> radicals can undergo further rearrangements with lower barriers, leading to direct OH radical reformation. Master equation simulations are used to predict OH radical reformation.

The ISOPO<sub>2</sub> radicals will also react with NO in the troposphere, producing alkoxyl radicals (RO) and isoprene nitrates (INs). There remain significant uncertainties around the yields of these INs. This talk will examine the potential for these INs to isomerize via novel ring-closing pathways to give unstaturated polycyclic orthonitrites. For the  $\delta$ -hydroxy INs, low-energy pathways to sixmembered ring compounds are available, with barriers around 15 kcal/mol below the respective RO<sub>2</sub> + NO reactants, or 10 kcal/mol below the RO + NO<sub>2</sub> dissociation products. In the  $\beta$ -hydroxy INs, isomerization forms five-membered ring orthonitrites. In addition to being potential new stabilization products of isoprene RO<sub>2</sub> + NO reactions, isomerization reactions can interconvert the identity of nitrate intermediates and thus the alkoxyl radical dissociation products.

Finally, new pathways identified in the photo-isomerization of the major isoprene oxidation products methyl vinyl ketone (MVK) and methacrolein (MACR) are also described. Although photo-dissociation of these species is known to be inefficient, light induced isomerization reactions may be significant at wavelengths longer than those required to achieve dissociation.

## REACTIVITY OF BIOGENIC VOLATILE ORGANIC COMPOUNDS WITH NO3 RADICAL

Bénédicte Picquet-Varrault\* LISA, UMR-CNRS 7583, Université Paris-Est Créteil et Université de Paris, 61 Avenue du Général de Gaulle, 94010 Créteil Cedex, FRANCE

Keywords

Atmospheric reactivity, night-time chemistry, NO<sub>3</sub>, biogenic VOC, aerosols, organic nitrates.

Biogenic Volatile Organic Compounds (BVOC) are highly emitted by vegetation and play a key role in atmospheric chemistry. They are very reactive towards atmospheric oxidants (OH, NO<sub>3</sub>, O<sub>3</sub>) and significantly contribute to the formation of Secondary Organic Aerosol (SOA) at the global scale (Brown and Stutz, 2012). In addition, night-time chemistry initiated by NO<sub>3</sub> radicals leads to the formation of organic nitrates which behave as reservoirs for reactive nitrogen (Mao et al., 2013). Hence, these processes affect air quality and climate through regional and global budgets for reactive nitrogen, ozone and organic aerosol (Ng et al., 2017). Despite the significance of this topic, the NO<sub>3</sub>+BVOC reactions remain poorly understood.

In this talk, we present an overview of the state of the art for  $NO_3$ +BVOC reactions together with new kinetic and mechanistic results obtained at LISA thanks to experiments in simulation chambers. These results will be discussed with a particular focus on the influence of the BVOC chemical structure on the reactivity (kinetic, SOA and organic nitrates formation).

## References

Brown SS, Stutz J. Nighttime radical observations and chemistry. Chem. Soc. Rev. 2012; 4: 6405-6447.

Mao J, Paulot F, Jacob DJ et al. Ozone and organic nitrates over the eastern United States: Sensitivity to isoprene chemistry. J. Geophys. Res. Atm. 2013; 118:11,256-11,268.

Ng NL, Brown SS, Archibald AT, et al. Nitrate radicals and biogenic volatile organic compounds: oxidation, mechanisms, and organic aerosol. Atmos. Chem. Phys. 2017; 17:2103-2162.

# **ORAL PRESENTATIONS**

## Accurately Predicting the Kinetics of Complex Reacting Systems: Status Report

William H. Green<sup>\*</sup> Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

Keywords

Combustion, Reaction Mechanism Generator, Modeling, Quantum Chemistry

For more than 80 years the kinetics community has been working to develop the ability to predict the rates and products of individual reaction steps and complete reaction networks. The first step is to identify all the important species and reactions; this can be done by hand or using automatic mechanism generation software. These finite mechanisms cannot include all the reactions occurring in the real system, so models built on them will suffer from mechanism truncation error. One way to try to minimize mechanism truncation error is to assess the potential importance of species and reactions using estimates, but this only works if the estimates are reliable. Recently machine learning has made it practical to make more reliable estimates based on much larger experimental and quantum chemistry datasets than were used in the past to determine thermochemical group values and linear free energy correlations for rate coefficients. For many systems it is impossible to determine all the rate coefficients experimentally, but quantum chemistry calculations can be used instead or to supplement the experimental data. In some cases the quantum chemistry calculations are nearly as accurate as experiments, and it is now possible (though challenging) to compute hundreds or thousands of parameters automatically. Sometimes models built this way allow accurate predictions even before any experiments are done. In this talk I summarize the current status of predictive chemistry, show some recent examples of successes, and identify some of the remaining challenges that need to be addressed to increase its scope, accuracy, and robustness.

## Revisiting the gas-phase rate coefficient of the $OH + SO_2 + M \rightarrow HSO_3 + M$ reaction

M.R. McGillen<sup>1,3,\*</sup> H. Elothmani<sup>1</sup>, Y. Ren<sup>1</sup>, L. Zhou<sup>1</sup>, M. Idir<sup>1</sup>, S. El Hajjaji<sup>2</sup>, V. Daële<sup>1</sup>, A.R. Ravishankara<sup>1,3,4,5</sup> and A. Mellouki<sup>1</sup>

<sup>1</sup>CNRS-INSIS, Institut de Combustion, Aérothermique, Réactivité et Environnement 1C, Avenue de la recherche scientifique, 45071 Orléans cedex 2, France

<sup>2</sup> Faculté des Sciences - Université Mohammed V, Rabat, Maroc

<sup>3</sup>Le Studium Loire Valley Institute for Advanced Studies, Orléans, France.

<sup>4</sup>Departments of Chemistry and Atmospheric Science, Colorado State University, Fort Collins, CO 80253, USA

<sup>5</sup>NOAA Earth System Research Laboratory (ESRL) Chemical Sciences Division, 325 Broadway, Boulder, CO

80305, USA

Keywords

Hydroxyl, Sulfur dioxide, Kinetics, Pressure dependence, Temperature dependence.

Oxidation of  $SO_2$  to sulfuric acid impacts acid precipitation and aerosol nucleation in Earth's atmosphere in remote and polluted environments. This oxidation can take place in both the liquid and gas phase. Only the gas phase oxidation is expected to lead to new particles because of the clustering reactions of  $H_2SO_4$ . This aerosol nucleation has a major effect upon air quality and the Earth's radiative balance, and is of crucial importance to the chemistry of the atmosphere.

The rate limiting step in this process is the reaction of OH radicals with  $SO_2$  to form  $HSO_3$ . The pressure- and temperature-dependent reaction of  $OH + SO_2$  has been studied many times previously – since its importance was first recognized in the 1970s. Notwithstanding, some of the most recent literature has cast doubt on much of this data, especially under conditions that are relevant to atmospheric chemistry.

Here, we present measurements of the rate coefficient using the pulsed laser photolysis–laser induced fluorescence technique as a function of temperature (249–373 K) and of pressure in helium, argon and nitrogen bath gases (30–600 Torr). In addition, relative rate measurements using a chamber at 760 Torr (N<sub>2</sub>, O<sub>2</sub> and air) were also performed to corroborate our absolute observations. By utilizing these new data, together with the available literature data, an updated pressure- and temperature-dependent parameterization will be provided. This allows the atmospheric impact of this reaction to be constrained with a new level of certainty.

## Deep Learning of Activation Energies and Automated Reaction Dataset Generation

Colin A. Grambow<sup>1</sup> and William H. Green \*1

<sup>1</sup>Department of Chemical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge, MA 02139, USA

Keywords

activation energy prediction, automated transition state search, chemical reaction database, deep learning, mechanism generation.

Automated mechanism generation is an efficient tool for rapidly constructing large-scale chemical reaction mechanisms, which are necessary for realistic modeling of complex processes, such as combustion and oxidation, soot formation, or pyrolysis. Nonetheless, hard-coded reaction templates employed by mechanism generation software do not cover the set of all possible reactions that might be important. Moreover, only a limited quantity of high-quality data is available for the estimation of kinetic rates during mechanism generation, which may result in poor estimates and the erroneous exclusion of important reactions. In response, we have developed methods to automatically generate a large database of chemical reactions and designed a template-free deep learning model capable of providing a quick assessment of potentially important reactions that are missing from a reaction mechanism.

We use activation energy as a temperature-independent measure to gauge the potential importance of new reactions and train a machine learning model to estimate the energies by relying on a reaction encoding which predominantly focuses on the atoms involved in the reactive center. In order to predict kinetically relevant activation energies as well as being able to tell which reactions have barriers that are so large that they cannot possibly be relevant, the training data for the machine learning model must span a more diverse set of reactions than is currently available in the literature. We use an automated transition state finding algorithm to generate a diverse training set of tens of thousands of reactions, and thus create an activation energy prediction model that can quantify the importance of proposed reactions.

\*Corresponding author: whgreen@mit.edu

## DMS H-ABSTRACTION BY OH IN EXCESS IN THE ABSENCE OF O<sub>2</sub>

Zoi Salta<sup>1</sup>, Jacopo Lupi<sup>1</sup>, Oscar N. Ventura<sup>2</sup> and Vincenzo Barone<sup>1</sup> <sup>1</sup> SMART, Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa, ITALY <sup>2</sup>CCBG, Detema, Facultad de Química, Isidoro de María 1614, 11800 Montevideo, URUGUAY

#### Keywords

DMS, DMSO, Atmospheric chemistry, Thiirane, Chemical reactivity, Rate constants.

The atmospheric sulfur cycle has been the subject of intensive investigation over a large period of time, mostly because of the need to continuously have an assessment of the contribution of anthropogenically produced sulfur to problems such as acid rain, visibility reduction, and climate modification. Dimethyl sulfide (DMS) accounts for approximately 60% of the total natural sulfur gases released into the atmosphere and its reactions with the 'OH radical during daytime leads to the formation of a variety of sulfur-containing end products, with one of the most important species being dimethyl sulfoxide (CH<sub>3</sub>S(O)CH<sub>3</sub>), DMSO). The essential initial reactions are i) H-abstraction from the methyl groups, which produces a very important atmospheric species, the methyl thiyl radical (CH<sub>3</sub>S<sup> $\bullet$ </sup>), and ii) 'OH addition to the sulfur atom, from which DMSO is assumed to emerge after reaction with O<sub>2</sub>.

In this work, we used quantum chemical procedures – DFT, CCSD(T) and composite methods – to investigate the potential energy surface (PES) of the reaction of DMS with 'OH, when the latter is in excess and no  $O_2$  is present. Initial pre-reactive complexes (PRCs) for addition and abstraction were found at -9.0 and -4.4 kcal/mol respectively (G4 results). The methyl thiomethylene radical (MTMr) was obtained at -25.2 kcal/mol, and four important paths were identified on the PES, leading to products: DMSO (-99.6 kcal/mol), thiirane (-100.1 kcal/mol), CH<sub>3</sub>SH + CH<sub>2</sub>O (-97.3 kcal/mol) and CH<sub>3</sub>OH + CH<sub>2</sub>S (-85.8 kcal/mol). Two novel intermediates, methylsulfinyl methanol (MSMOH) and S-methylene methanesulfenic acid (SMMSA) were located at -111.1 and -72.9 kcal/mol respectively, with DMSO arising from the latter. Theoretical spectra of these species is discussed in comparison to those of DMS and DMSO.

Besides locating stable species and transition states, several rate constants were calculated, especially for the initial H-abstraction for which experimental data exist, as well as for the formation channels of the most stable final products. In the first case, the rate constant calculated at the CCSD(T)/cc-pVTZ// $\omega$ B97X-D/cc-pVTZ level with a value of 3.6 x 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, is in excellent agreement with the experimental one at 4.8 x 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

## Automated Networks: Harnessing Dynamics, Kinetics and Human Guided VR for Blackbox Mechanism Generation

Robin J Shannon<sup>1,2</sup>\*, Dmitrii V. Shalashilin<sup>2</sup> and David R Glowacki<sup>2</sup>,

<sup>1</sup>School of Chemistry, University of Bristol, BS8 1TS, UK <sup>2</sup>School of Chemistry, University of Leeds, LS2 9JT, UK

Keywords

Mechanism generation, Automation, Statistical rate theory, Electronic structure theory, Virtual Reality

Exploring reactive networks is a fundamental problem across all aspects of chemistry. From complex combustion or atmospheric models to conformational networks in proteins to novel synthetic routes in organic chemistry, there is a strong need to automate the exploration of networks of reactions that the given system can undergo. Building upon two recent theoretical advances (Shannon 2018) we present a combined molecular dynamic, master equation framework for generating reaction networks in a black box manner using the kinetics of the system in question to guide the search of chemical space. This framework is implemented in the open source ChemDyME software and this presentation will briefly demonstrate the application of this code to a well benchmarked combustion system

Additionally, we have been implementing aspects of the ChemDyME framework within the virtual reality environment in the open source Narupa dynamics code (O'Connor 2019) allowing humans in VR to guide molecular reactions in a game-like environment. Gamification of science is a burgeoning field and this talk will end with some initial insights on human versus computer strategies for exploring chemical space.



## References

Shannon RJ, Glowacki DR, J. Phys. Chem. A 122, 6, 1531, 2018

Shannon RJ, Amabilino S, O'Connor M, Shalashilin DV, Glowacki DR. J. Chemical Theory and Computation, 14, 9, 4541-4552, 2018

O'Connor M, Bennie SJ, Deeks HM, Jamieson-Binnie A, Jones AJ, et al. arXiv:1902.01827, 2019

\*robin.shannon@bristol.ac.uk

# KINETIC AND MECHANISTIC STUDY OF THE REACTION $\label{eq:ch3} CH_3SO_2NH_2 + OH$

Matias Berasategui<sup>1,\*</sup>, Damien Amedro<sup>1</sup>, Achim Edtbauer<sup>1</sup>, Jonathan Williams<sup>1,2</sup> and John Crowley<sup>1</sup> <sup>1</sup>Division of Atmospheric Chemistry, Max-Planck-Institut für Chemie, Mainz, 55128, Germany <sup>2</sup>Energy, Environment and Water Research Center, The Cyprus Institute, Nicosia, Cyprus

Keywords

Sulfonamides, FTIR, Rate constant, Atmospheric Oxidation, Lifetime, Marine Emission, VOC.

**Introduction.** Methanesulfonamide,  $CH_3SO_2NH_2$ , has recently been detected in ambient air for the first time, with up to 150 pptv found in air over the Arabian Sea during the 2017 AQABA campaign (Air Quality in the Arabian BAsin). In the present work we study the possible fate of this compound in the atmosphere and calculate the residence time from the kinetic study of the reaction  $CH_3SO_2NH_2 + OH$ .

**Experimental.** The rate coefficient,  $k_1$ , for the reaction between OH and CH<sub>3</sub>SO<sub>2</sub>NH<sub>2</sub> was studied using the relative rate method in a 44.39 L cylindrical quartz-wall chamber equipped with a White-type mirror system (86.3 m optical path) at room temperature (298.2 K) and 700 Torr of total pressure (in Air). OH was generated by the photolysis of O<sub>3</sub> (254 nm) in the presence of H<sub>2</sub>, the depletion of CH<sub>3</sub>SO<sub>2</sub>NH<sub>2</sub> and the reference reactants (CH<sub>3</sub>OH, HC(O)OH and CH<sub>3</sub>C(O)CH<sub>3</sub>) was followed by FTIR spectroscopy (resolution = 2 cm<sup>-1</sup>, 128 scans). Products were also observed by FTIR.

**Results.**  $k_1$ , was derived by analysis of the time dependence of absorption bands at 856, 1170, 1383 and 3450 cm<sup>-1</sup> in three different experiments (Figure 1). Within experimental uncertainty, all three reference reactants yielded the same rate coefficient with  $k_1 = (1.4 \pm 0.2) \times 10^{-13}$  cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup>.

Along with the vibrational characterization of  $CH_3SO_2NH_2$  in the gas-phase, the products of the reaction with OH were identified using reference spectra. The main products were: CO, CO<sub>2</sub>, HNO<sub>3</sub>, N<sub>2</sub>O and SO<sub>2</sub>. Small amounts of NO<sub>2</sub> and HC(O)OH were also observed. These products are consistent with the following mechanism with initial H-abstraction at the CH<sub>3</sub> group:

$$CH_3SO_2NH_2 + OH \rightarrow CH_2SO_2NH_2 + H_2O$$

$$CH_2SO_2NH_2 + O_2 \rightarrow O_2CH_2SO_2NH_2$$

$$2 O_2CH_2SO_2NH_2 \rightarrow OCH_2SO_2NH_2 + O_2$$

$$OCH_2SO_2NH_2 \rightarrow CH_2O + SO_2 + NH_2$$



Under our experimental conditions, CH<sub>2</sub>O and NH<sub>2</sub> are converted to mainly CO, CO<sub>2</sub>, HNO<sub>3</sub> and N<sub>2</sub>O.

(1)

(2)

(3)

(4)

**Conclusion.** Our results indicate a lifetime of methanesulfonamide in the atmosphere of 2-3 months with respect to OH ( $\approx 10^6$  molecule cm<sup>-3</sup>) if this is the only loss process. This will help constrain estimates of its oceanic source strength.

## Model Analysis Based Experimental Design for Combustion Kinetics

Bin Yang<sup>\*</sup>, Jiaxing Wang and Zijun Zhou Tsinghua University, 100084 Beijing, CHINA

#### Keywords

Combustion Kinetic Model, Uncertainty Quantification, Experimental Design, Model Similarity.

The need for reliable chemical kinetic models is critical in scientific understanding combustion processes, and has led to the recent proliferation in the development of detailed and reduced chemical kinetic models for hydrocarbons and biofuels. Useful as these contributions are, the model predictions still have large uncertainties, which mainly come from the uncertainties of model structure and input parameters, especially those of the rate coefficients of elementary reactions. To reduce these uncertainties, reliable data from fundamental combustion experiments are essential. In this talk, some strategies will be demonstrated on how to design the combustion experiments with rich kinetic information, which will be used for model development and optimization. Emphasis will be put on several experimental design methods including sensitive entropy analysis (Li et al., 2017) and surrogate model similarity analysis (Wang et al. 2018). A computational platform named CombustionUQ which includes the combination of several available strategies is developed, and some combustion reaction systems will be employed as examples to illustrate these methods.

## References

Wang JX, Li S, Yang B. Combustion kinetic model development using surrogate model similarity method. Combust. Theor. Model. 2018;22:777-794.

Li S, Tao T, Wang J, Yang B, Law CK, Qi F. Using sensitivity entropy in experimental design for uncertainty minimization of combustion kinetic models. Proc. Combust. Inst. 2017:36:709-716,

## **EMPLOYING PULSED IRRADIATION IN PHOTOCATALYSIS**

Thomas P. Nicholls<sup>1</sup>, Johnathon C. Robertson<sup>1</sup> and Alex C. Bissember<sup>1,\*</sup> <sup>1</sup>School of Natural Sciences – Chemistry, University of Tasmania, Hobart, Tasmania 7001, AUSTRALIA

Keywords

copper, photocatalysis, homogeneous catalysis, pulsed LED irradiation, multiphase circuits.

The establishment of original methods for the direct functionalization of organic molecules can simplify and shorten synthetic routes, enhance efficiency, and contribute to making valuable compounds more accessible. Our work has explored strategies that aim to expand the scope of first row transition metal-based catalysts in photoredox catalysis (Nicholls et al., 2016). Recognizing the capacity for pulsed light-emitting diode (LED) irradiation to enhance photosynthetic activity and phytochemical production in plants (Tennessen et al., 1995), we postulated that pulsed irradiation strategies may have broader implications in organic synthesis. Recently, we demonstrated that pulsed irradiation enhances both the rate and yield of a photocatalyzed reaction for the first time (Nicholls et al., 2018). This research was facilitated by our development of new technology (a multiphase circuit) that provides precise control of the power and pulse frequency of LED irradiation and duty-cycle modulation. Our studies and progress in these areas will be presented.



## References

Tennessen DJ, Bula RJ, Sharkey TD. Efficiency of photosynthesis in continuous and pulsed light emitting diode irradiation. Photosynth Res 1995; 44: 261-269.

Nicholls TP, Constable GC, Robertson JC, Gardiner MG, Bissember AC. Brønsted Acid Cocatalysis in Copper(I)-Photocatalyzed  $\alpha$ -Amino C–H Bond Functionalization. ACS Catal 2016; 6: 451-457.

Nicholls TP, Robertson JC, Gardiner MG, Bissember AC. Identifying the potential of pulsed LED irradiation in synthesis: copper-photocatalysed C–F functionalisation. Chem Commun 2018; 54: 4589-4592.

## **BENCHMARKING DFT FOR COMPUTATIONAL KINETICS**

Marc E. Segovia<sup>1</sup>, Oscar N. Ventura<sup>1\*</sup>, Jacopo Lupi<sup>2</sup>, Zoi Salta<sup>2</sup>, Nicola Tasinato<sup>2</sup> and Vincenzo Barone<sup>2</sup>

<sup>1</sup>CCBG, Detema, Facultad de Química, Isidoro de María 1614, 11800 Montevideo, URUGUAY <sup>2</sup> Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa, ITALY

Keywords

Benchmark, Density Functional Theory, H<sub>2</sub>S, Atmospheric Chemistry, Chlorine.

DFT methods are the computational tools of choice for the study of molecular species and reaction mechanisms of some complexity. Many studies assessed their accuracy with respect to geometries, atomization energies, reaction and formation enthalpies, dipole moments and other molecular properties (Mardirossian, 2017). However, there is less information about their use for the determination of rate constants. Previous information suggests the paradoxical situation that *less* sophisticated methods and *small* basis sets seem to be the best choice for this task.

In this work, we have studied the reaction  $H_2S + Cl \rightarrow HS + HCl$ , the experimental rate constant of which range from 2.2 to 11.2 x  $10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Few theoretical calculations exist (Alecu, 2009; Resende, 2008), spanning the range of 0.28 to 250 x  $10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, with the best values (from 4 to 12 x  $10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) obtained by (Alecu, 2009) at the CCSD(T)//QCISD(T)/CBS level. In this work we used the CCSDT(Q,Full)/CBS//CCSD (T,Full)//CBS with correlation consistent core-valence basis sets to calculate the species in this reaction channel. The values of the well depth for the pre-reactive complex, the energy difference of the TS with respect to the reactants, and the potential energy barrier, were used as parameters to assess the fitness of different DFT methods for describing the reaction. BLYP, PBE, BHandHLYP, PBE1, M06, M06-2X, BMK, THCTHHYB, MPWB95, MPWB1K, WB97XD and B2PLYP were tested with Pople's basis sets up to 6-311++G(3df,2pd) and Dunning's basis sets (aug)cc-pVnZ, with n=D,T,Q, and 5. Valence only MP2, QCISD(T) and CCSD(T) methods were also used as examples of current post-Hartree-Fock procedures.

The best combination of DFT method and basis sets, according to these criteria, were used to calculate the rate constant for the reaction. BMK, WB97XD and MPWB1K methods gave the best results (from 3.3 to  $7.2 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) *provided that small basis sets were used* (especially 6-31G(d) and 6-31G(d,p)). CCSD(T)/cc-pVTZ//QCISD/aug-cc-pVTZ calculations gave also an accurate value of this rate constant, 6.6 x x 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The possible generalization of this research to other systems is discussed.

### References

Alecu IM. Kinetic studies and computational modeling of atomic chlorine reactions in the gas phase. Dissertation for the Degree of PhD, University of North Texas, 2009.

Mardirossian N, Head-Gordon M. Thirty years of density functional theory in computational chemistry: an overview and extensive assessment of 200 density functionals. Mol. Phys. 2017;115:2315-2372.

Resende SM, Pliego, Jr., JR, Vandresen, S. Ab initio study of the Cl+H<sub>2</sub>S atmospheric reaction: is there a breakdown of the transition state theory? Mol. Phys. 2008;106:841-848.

\*Corresponding author: Oscar.N.Ventura@gmail.com

## TEMPERATURE AND PRESSURE DEPENDENCE OF THE KINETICS OF THE CH<sub>2</sub>OO + CH<sub>3</sub>OO REACTION

Rabi Chhantyal-Pun,<sup>1\*</sup> Nicholas Zachhuber,<sup>1</sup> Rebecca Martin,<sup>1</sup> M. Anwar H. Khan,<sup>1</sup> Dudley E. Shallcross<sup>1</sup> and Andrew J. Orr-Ewing<sup>1</sup> <sup>1</sup>University of Bristol, School of Chemistry, Cantock's Close, Bristol BS8 1TS, United Kingdom

Keywords

Criegee Intermediates, Peroxy Radicals, Kinetics, Particle Formation, Aerosols

Criegee intermediates and peroxy radicals are both important intermediates produced during the oxidation of volatile organic compounds (VOCs) in the atmosphere. Criegee intermediates form during the ozonolysis of alkenes, whereas peroxy radicals are generated by OH initiated oxidation of various VOCs. Recently, the reaction of Criegee intermediates with peroxy radicals was predicted to be barrierless and to produce an adduct peroxy radical, resulting in initiation of an oligomerization process.<sup>1,2</sup> Thus, these reactions may lead to particle formation in the troposphere. A chamber study by Finlayson-Pitts and co-workers reported production of oligomers with Criegee intermediate chain units during ozonolysis of trans-3-hexene in the presence of OH radicals, likely due to Criegee intermediate + peroxy radical reactions.<sup>3</sup> The rate of reaction of the simplest Criegee intermediate, CH<sub>2</sub>OO, with the simplest alkyl peroxy radical, CH<sub>3</sub>OO, was measured using time resolved cavity ring-down spectroscopy under tropospherically relevant conditions of temperature (250 - 310 K) and pressure (20 to 100 Torr, N<sub>2</sub>). CH<sub>3</sub>OO was produced by photolysis of acetone and measured in-situ by observation of NO<sub>2</sub> from the CH<sub>3</sub>OO + NO reaction in complementary experiments. The rate coefficients obtained from these measurements were coupled into a global atmospheric chemistry and transport model, and preliminary predictions of the impact will also be presented.

## References

<sup>1</sup>Vereecken L, Harder H, Novelli A. The Reaction of Criegee Intermediates with NO, RO<sub>2</sub>, and SO<sub>2</sub>, and their Fate in the Atmosphere. Phys Chem Chem Phys 2012:14:14682-14695

<sup>2</sup>Miliordos E, Xantheas SS. The Origin of the Reactivity of the Criegee Intermediate: Implications for Atmospheric Particle Growth. Angew Chem Int Ed 2015:54:1-6

<sup>3</sup>Zhao Y et al. Role of the Reaction of Stabilized Criegee Intermediates with Peroxy Radicals in Particle Formation and Growth in Air. Phys Chem Chem Phys 2015:17:12500-12514

## Ketohydroperoxide reactions uncovered by KinBot

Ruben Van de Vijver<sup>1</sup>, Judit Zádor<sup>2</sup>, Guy B. Marin<sup>1</sup> and Kevin M. Van Geem<sup>1,\*</sup> <sup>1</sup>Laboratory for Chemical Technology, Ghent University, Ghent, Belgium <sup>2</sup>Combustion Research Facility, Sandia National Laboratories, Livermore, CA, USA

#### Keywords

Potential Energy Surface, Combustion, Ketohydropreoxide, Automation

Ketohydroperoxide species are important intermediates in low-temperature combustion and a detailed understanding of the branching fractions of their monomolecular reactions is key to describe the formation of many products. Recently, two articles have focused on the automatic search for the reactions of the smallest  $\gamma$ -ketohydroperoxide, i.e. 3-hydroperoxypropanal.<sup>1,2</sup> They have used several tools such as the freezing string method, single- and double-ended searches, KinBot and the single-component artificial force induced reaction method. In the first article<sup>1</sup>, 75 unique pathways were identified, and in the second article<sup>2</sup>, 85 channels are reported.

Recently, a new version of the KinBot software has been developed with an improved list of reaction families, and also including a combinatorial reaction search. The latter considers all combinations of breaking n bonds and forming n new ones. The value of n is user defined and was set to a maximum of 3 in this work. KinBot has been applied to search reactions for 3-hydroperoxypropanal. All reactions previously found were also identified by KinBot. Additionally, KinBot was able to identify several reaction pathways previously not reported, of which two examples are shown in Figure 1.



Figure 1: Two examples of new reactions found by KinBot: a 3-membered ring formation with elimination of  $O_2$  and a carbine formation pathway.

#### References

1. Grambow, C. A.; Jamal, A.; Li, Y.-P.; Green, W. H.; Zádor, J.; Suleimanov, Y. V. Journal of the American Chemical Society 2018, 140, 1035-1048.

2. Maeda, S.; Harabuchi, Y. Journal of Chemical Theory and Computation 2019, 15, 2111-2115.
## KINETIC STUDIES OF SELF- AND CROSS-REACTIONS OF SMALL PEROXY RADICALS IN THE HIGHLY INSTRUMENTED REACTOR FOR ATMOSPHERIC CHEMISTRY

Freja F. Østerstrøm<sup>1,\*</sup>, Lavinia Onel<sup>1</sup>, Alexander Brennan<sup>1</sup>, Joseph Parr<sup>1</sup>, Ellie Cooke<sup>1</sup>,

Lisa Whalley<sup>1,2</sup>, Paul W. Seakins<sup>1,2</sup>, and Dwayne E. Heard<sup>1,2</sup>

<sup>1</sup> School of Chemistry, University of Leeds, LS2 9JT, Leeds, United Kingdom

<sup>2</sup> National Centre for Atmospheric Science, University of Leeds, LS2 9JT, Leeds, United Kingdom

#### Keywords

Gas phase kinetics, Atmospheric chemistry, Laser induced fluorescence, Simulation chamber, Peroxy radicals.

Peroxy (RO<sub>2</sub>) radicals are highly reactive species critical in most atmospheric oxidation; formed in the degradation of volatile organic compounds they can lead to O<sub>3</sub> and aerosol formation in the atmosphere, making them central molecules to understand. The most abundant RO<sub>2</sub> radicals in the atmosphere are predicted to be CH<sub>3</sub>O<sub>2</sub> and C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>, however their ambient concentrations are not yet measured. Under low NOx conditions (e.g. in remote areas) the daytime chemistry of CH<sub>3</sub>O<sub>2</sub> and C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> is dominated by their self-reactions and the reactions with HO<sub>2</sub> or other RO<sub>2</sub> radicals present. Given the intermediate nature of RO<sub>2</sub> radicals, direct detection is challenging.

A selective and sensitive method adapted from laser induced fluorescence (LIF) spectroscopy, fluorescence assay by gas expansion (FAGE), was developed at the University of Leeds and used in this study for the detection of CH<sub>3</sub>O<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> and HO<sub>2</sub> radicals by their conversion to CH<sub>3</sub>O, C<sub>2</sub>H<sub>5</sub>O, and OH, respectively, in an excess of NO (Heard and Pilling, 2003, Onel et al., 2017). Subsequently CH<sub>3</sub>O, C<sub>2</sub>H<sub>5</sub>O, and OH radicals are detected by FAGE. Experiments investigating the self- and cross-reactions of the RO<sub>2</sub> radicals were performed in the highly instrumented reactor for atmospheric chemistry (HIRAC) (Glowacki et al., 2007). A second FAGE based method, ROxLIF, has been developed measuring the sum of RO<sub>2</sub> radicals by conversion of the RO<sub>2</sub> species to HO<sub>2</sub> in the presence of NO and CO, before reaching the FAGE cell where HO<sub>2</sub> is detected by conversion to OH with excess added NO. The self-reactions of the RO<sub>2</sub> radicals were studied using ROxLIF sampling from HIRAC in addition to the FAGE method.

The decays of the radicals using both methods were used to obtain kinetic data for different reactions; for example the self-reactions of  $CH_3O_2$  and  $C_2H_5O_2$  and the cross-reaction of  $CH_3O_2$  with HO<sub>2</sub>. The preliminary results are overall in agreement with IUPAC and JPL recommended values, but improving the uncertainties and validating the two methods used in the experiments.

#### References

Heard DE, Pilling MJ. Measurement of OH and HO<sub>2</sub> in the Troposphere. Chem Rev 2003;103:5163-5198.

Glowacki DR, Goddard A, Hemavibool K, Malkin TL, Commane R, Anderson F, Bloss WJ, Heard DE, Ingham T, Pilling MJ, Seakins PW. Design of and initial results from a Highly Instrumented Reactor for Atmospheric Chemistry. Atmos Chem Phys 2007;7:5371-5390.

Onel L, Brennan A, Seakins PW, Whalley L, Heard DE. A new method for atmospheric detection of the CH<sub>3</sub>O<sub>2</sub> radical. Atmos Meas Tech 2017;10:3985-4000.

\*Corresponding author: freja.oesterstroem@gmail.com

## ELEMENTARY-REACTION KINETICS FOR CELLULOSE AND HEMICELLULOSE PYROLYSIS

Phillip R. Westmoreland,\* Arnab Bose, Charles J. McGill, Amrutha Raghu Chemical and Biomolecular Engineering Department, North Carolina State University, Raleigh, NC 27695-7905, USA

#### Keywords

Pyrolysis, biomass, computational chemistry, measurement, catalysis.

Pyrolysis kinetics of cellulose and hemicellulose has become understandable at an elementaryreaction level due to recent data and quantum-chemical modeling. In Seshadri and Westmoreland (2012), we had modeled glucose pyrolysis and compared to data. We found that the elementary steps of cellulose breakdown were all concerted pericyclic reactions, apparently catalyzed by the hydroxyl groups of other glucose molecules, H<sub>2</sub>O, and intermediates. By extending this glucose modeling, we proposed that cellulose pyrolysis could be self-catalyzed by intimate contact of cellulose chains and their hydroxyls in the solid phase and melt. This hypothesis has recently been supported by experiments and modeling in the Dauenhauer group (Maliekkal et al., 2019). Likewise, gas-phase anomerization of monosaccharides has been proposed to proceed by concerted reactions (McGill and Westmoreland, 2019).

The chemical composition of hemicellulose (multiple monomers, side chains, and branching) is much more varied that of cellulose, complicating the kinetics, but the amorphous physical nature of hemicellulose is even better suited to decomposition by hydroxyl self-catalysis than is crystalline cellulose. Our calculations for xylose and xylan and our measurements by twodimensional GCxGC-TOFMS reveal numerous pathways that can occur. A new approach is to examine the problem with Reactive Molecular Dynamics (Raghu, 2019), which successfully predicts a number of the experimental products.

#### References

Seshadri V, Westmoreland PR. Concerted Reactions and Mechanism of Glucose Pyrolysis and Implications for Cellulose Kinetics. J. Phys. Chem. A 2012;116(49):11997-20013.

Maliekkal V, Maduskar S, Saxon DJ, Nasiri M, Reineke TM, Neurock M, Dauenhauer P. Activation of Cellulose via Cooperative Hydroxyl-Catalyzed Transglycosylation of Glycosidic Bonds. ACS Catalysis 2019;9:1943-1955.

C.J. McGill, P.R. Westmoreland, "Monosaccharide Isomer Interconversions Become Significant at High Temperatures," J. Phys. Chem. A 2019;123(1):120–131.

Raghu A. Reaction Paths for Hemicellulose Pyrolysis using Reactive Molecular Dynamics. M.S. Thesis, Raleigh, NC: North Carolina State University; 2019. 76 p.

## DEVELOPMENT AND VALIDATION OF A NEW EXPERIMENTAL SET-UP TO STUDY REACTIONS BETWEEN PEROXY RO<sub>2</sub> AND HO<sub>X</sub> RADICALS

<u>F. Kravtchenko<sup>1\*</sup></u>, L. Pillier<sup>1</sup>, S. Batut<sup>1</sup>, B. Calimet<sup>2</sup> and C. Fittschen<sup>1</sup>

 <sup>1</sup> Univ. Lille, CNRS, UMR 8522 - PC2A - Physicochimie des Processus de Combustion et de l'Atmosphère, F-59000 Lille, France
 <sup>2</sup> Univ. Lille, CERLA - Centre d'Etudes et de Recherches Lasers et Applications, F-59000 Lille, France

Keywords

Atmospheric chemistry, peroxy radicals, HOx radicals, Laser Induced Fluorescence, cw-CRDS.

In the atmosphere, organic pollutants such as Volatile Organic Compounds (VOCs) from biogenic or anthropogenic sources are photochemically oxidized and lead to the formation of peroxy radicals HO<sub>2</sub> and RO<sub>2</sub>, which play a major role in tropospheric chemistry. The reactivity of RO<sub>2</sub> and HO<sub>x</sub> (HO<sub>2</sub> and OH) radicals controls the oxidative capacity of the atmosphere and the formation of tropospheric ozone and secondary pollutants. However, it is still poorly known and subject to controversy in the literature, especially in clean environments containing low NOx concentrations (remote regions: marine boundary layer or tropical forest). The uncertainties and/or lack of data on RO<sub>2</sub>+HO<sub>x</sub> reactions rates and branching ratios can lead to important errors on modelling of ozone and radical concentrations in the atmosphere. New experimental results, with a more detailed characterization of radicals and products, are then clearly needed.

The aim of the present work is the development of a new and unique experimental device to study reactions between  $RO_2$  and  $HO_x$  (rate constants and branching ratio measurements). The new setup consists of a fast flow tube coupled to three complementary techniques:

- Laser Induced Fluorescence (LIF) for in-situ OH radical measurements,
- continuous wave Cavity Ring-Down Spectroscopy (cw-CRDS) for HO<sub>2</sub> radical measurements,
- Mass Spectrometry with Molecular Beam sampling (MB/MS) for measurement of stable reaction products and radical species.

We will present the validation of the system through the study of different reactions between alkanes (ethane, propane) + OH, alcohol (methanol) + OH and CO + OH. Two different reactions were used for OH generation in the reactor:  $F+H_2O$  and  $H+NO_2$ . Unexplained OH recycling within the reactor was observed for all reaction partners (except CO) when using  $F + H_2O$  as precursor. This was confirmed by using deuterated reaction partners, i.e.  $CH_3OD + OH$  leads to OD formation while  $CH_3OH + OD$  leads to OH formation.

## A systematic kinetic modelling study of mono-aromatic hydrocarbons: towards the definition of reaction classes and rate rules.

Matteo Pelucchi<sup>1\*</sup>, Luna Pratali Maffei<sup>1</sup>, René Daniel Büettgen<sup>2</sup>, Warumporn Pejpichestakul<sup>1</sup> Carlo Cavallotti<sup>1</sup>, Alessio Frassoldati<sup>1</sup>, Karl Alexander Heufer<sup>2</sup>, Tiziano Faravelli<sup>1</sup>

<sup>1</sup>CRECK Modeling Lab, Department of Chemistry Materials and Chemical Engineering, Politecnico di Milano, Piazza Leonardo da Vinci 33, 20133, Milan, ITALY
<sup>2</sup>Physico Chemical Fundamentals of Combustion (PCFC), RWTH Aachen University, Schinkelstraße 8, 52062 Aachen, GERMANY

#### Keywords

Aromatics, Oxygenated Aromatics, Kinetics, Reaction Classes, Rate Rules

Aromatic hydrocarbons such as toluene represent a large fraction of commercial fuels such as gasoline, diesel and jet fuels. Oxygenated aromatic hydrocarbons such as anisole, guaiacol, catechol and vanillin (Pelucchi et al., 2019) are key components in surrogate models for biooils from the fast pyrolysis of biomass. As from the hierarchical nature of combustion, aromatic species such as benzene are also key building blocks in molecular growth kinetics leading to the formation of PAHs and particulate matter (soot). Moreover, oxygenated aromatics such as phenol are key intermediate in the oxidation of species such as benzene and toluene. Despite the relevant role played by aromatic and oxygenated aromatic hydrocarbons in combustion systems, to the best of our knowledge, no effort concerning the definition of reaction classes to be included in kinetic models for the pyrolysis and oxidation of such species has been reported in the literature so far. Moving from previous assessment of benzene (Pejpichestakul et al., 2019), toluene (Pelucchi et al., 2018), phenol (Pratali Maffei et al., 2019) anisole, catechol, guaiacol and vanillin (Pelucchi et al., 2019) pyrolysis and oxidation, and from recent systematic ignition delay time measurements in shock tubes and rapid compression machines (Büttgen et al., 2019) this work addresses the generalization of reaction classes and rate rules for aromatic species with single substitution (Figure 1), providing a solid basis for the extension to species with multiple substitution and more than one aromatic ring.



Figure 1: general structure of aromatic species with single substitution. R=H, CH<sub>3</sub>.

#### References

Büttgen RD, Pratali Maffei L, Pelucchi M, Faravelli T, Frassoldati A, Heufer KA, European Combustion Meeting, Lisbon, Portugal, 2019.

Pejpichestakul W, Ranzi E, Pelucchi M, Frassoldati A, Cuoci A, Parente A, Faravelli T, Proceedings of the Combustion Institute 37.1 (2019): 1013-1021.

Pelucchi M, Cavallotti C, Faravelli T, Klippenstein SJ, Physical Chemistry Chemical Physics, 2018

Pelucchi M, Cavallotti C, Cuoci A, Frassoldati A, Faravelli T, Ranzi E, Reaction Chemistry and Engineering, 2019

Pratali Maffei L, Pelucchi M, Faravelli T, Cavallotti C, International Conference on Chemical Kinetics, Orléans, France, 2019.

\*Corresponding author: matteo.pelucchi@polimi.it

## REACTIVITY OF OH RADICALS TOWARDS CH<sub>3</sub>CHO AT T<200 K: IMPLICATIONS IN ASTROCHEMISTRY

Sergio Blázquez<sup>1</sup>, Daniel González<sup>1</sup>, Bernabé Ballesteros<sup>1,2</sup>, André Canosa<sup>3</sup>, José Albaladejo<sup>1,2</sup> and Elena Jiménez<sup>1,2,\*</sup>

<sup>1</sup>Departamento de Química Física, Facultad de Ciencias y Tecnologías Químicas, Universidad de Castilla-La Mancha, Avda. Camilo José Cela 1B, 13071 Ciudad Real, SPAIN
 <sup>2</sup>Instituto de Investigación en Combustión y Contaminación Atmosférica, Edificio Polivalente, Camino de Moledores s/n, 13071 Ciudad Real, SPAIN
 <sup>3</sup>Département de Physique Moléculaire, Institut de Physique de Rennes, UMR CNRS-UR1 6251, UNIVERSE CONTRUCTION DE CONTR

Université de Rennes 1, Campus de Beaulieu, 263 Avenue du Général Leclerc, 35042 Rennes Cedex, France.

#### Keywords

Gas-phase reactivity, ultra-low temperature, CRESU technique, interstellar medium

Acetaldehyde (CH<sub>3</sub>CHO) has been observed in many sources of the interstellar medium (ISM) such as Sagittarius B2 molecular cloud (Nummelin et al., 2000), hot corinos (Laporte et al., 2019) or prestellar cores (Vastel et al., 2014). As hydroxyl (OH) radicals are ubiquitous in many interstellar environments, the gas-phase kinetics of the OH + CH<sub>3</sub>CHO reaction is important to be known at the ultra-low temperatures of the ISM (T~10-100 K). To date, the only determination of the rate coefficient, k(T), below 200 K for the title reaction was carried out by Vöhringer-Martínez et al. (2007) at 60, 77, 106 and 118 K. These authors observed an increase of k(T) with respect to that at room temperature ( $k(295 \text{ K})=1.5\times10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ) of ~5 times at 60 K and ~2 at T>100 K. A catalytic effect of H<sub>2</sub>O (increase of ~2 at all temperatures) was also observed by Vöhringer-Martínez et al. (2007).

In this work, the temperature dependence of k(T) for the OH+CH<sub>3</sub>CHO reaction in the absence of added water has been determined between 21.7 K and 177.5 K. The uniform supersonic expansion technique for cooling the gas is coupled to the pulsed laser photolysis/laser induced fluorescence kinetic technique (Jiménez et al., 2015). The reactivity of OH towards CH<sub>3</sub>CHO is greatly enhanced at 21.7 K ( $3.8 \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup>). This result will have an impact on modelling the depletion of this aldehyde in the ISM. The potential pressure dependence of k(T) has been measured at several temperatures.

#### References

Nummelin A et al. A three-position spectral line survey of Sagittarius B2 between 218 and 263 GHz. II. Data analysis. ApJ Supplement Series 2000; 128:213-243.

Jiménez E et al. Development of a pulsed uniform supersonic gas expansion system based on an aerodynamic chopper for gas phase reaction kinetic studies at ultra-low temperatures. Rev Sci Instrum 2015; 86:45108, 1–17.

Laporte CFP et al. MNRAS 2019; 483:1427-1436.

Vastel C et al. The origin of complex organic molecules in prestellar cores. ApJ Letter 2014; 795:L2.

Vöhringer-Martínez E et al. Water Catalysis of a Radical-Molecule Gas-Phase Reaction. Science 2007; 315:497-501.

## MECHANISTIC STUDY OF THERMAL DEGRADATION OF $\beta$ -1, 4-D-XYLAN

Matieyendou Goussougli\*, Baptiste Sirjean, Pierre-Alexandre Glaude,

René Fournet

Laboratoire Réactions et Génie des Procédés, Université de Lorraine, CNRS, F-54000 Nancy, France

Keywords: Energy, hemicellulose, pyrolysis, mechanism, electronic calculations.

The rapid increase of the world's population and of the global demand for energy constrain the use and availability of energy. The degradation of the environment and the depletion of fossil fuels push our societies to move towards alternatives to coal and oil, such as biomass. The development of thermochemical conversion processes of biomass requires kinetic models able to accurately predict the nature and quantities of products. Few (semi) detailed mechanisms are available up to now, which are based on global reactions to describe the primary decomposition of the constituents of biomass (cellulose, hemicellulose or lignin) and usually contains rate constants adjusted to experimental data. Recently, several theoretical studies have been performed about elementary reactions involved in the thermal decomposition of model molecules representative of hemicellulose (Huang et al. 2017, Lu et al. 2018). In this work, we investigate the main decomposition pathways of the basic structure of hemicellulose, *i.e.* β-1,4-D-xylan, up to the formation of the major volatiles species observed in experimental studies. This mechanism involves a propagation reaction, based on molecular reactions, which consume the initial polymer into volatile products. Theoretical calculations methods were used to investigate reaction channels and to determine the corresponding rate constants. The optimization and frequency calculation were performed at the B3LYP/6-311++G(d,p) level of theory, while the energy calculation was done at the same level as that considered in the CBS-QB3 method. ThermRot software was used to determine the rate parameters and the thermodynamic data. All possible reactions of the reactant and of new product were systematically investigated and the pathways associated with higher energy barriers were eliminated. This approach allowed to propose new reaction routes, whereas some reaction pathways proposed by Zhou et al (2018) could be discarded. The results show that the polymer can be initially depolymerized by two types of reactions depending of the position considered in the polymer. For midchain, a four-centered molecular reaction transferring a H atom, leads to the formation of four possible fragments, which in turn react to give volatiles species and other polymer fragments. For end chain, an easy ring opening may occur, leading to fragments and volatiles that are already involved in the midchain mechanism. Finally, the formation of volatiles species such as formic acid, furfural, formaldehyde, hydroxyacetaldehyde or acetaldehyde can be explain by this mechanism.

#### References

Li Z., Liu C., Xu X., Li Q. Computational and Theoretical Chemistry 2017, 1117, 130-140 Lu Q., Hu B., Zhang Z., Wu Y., Cui M., Liu D., Dong C., Yang Y., Combustion and Flame 2018, 198, 267-277

Zhou X., Li W., Mabon R., Broadbelt L. J., Energy & Environmental Science 2018, 11, 1240-1260

\*Corresponding author: matieyendou.goussougli@univ-lorraine.fr

#### Pressure-Dependent Rate Constant Caused by Tunneling Effects: OH + HNO<sub>3</sub> as an Example

<u>Thanh Lam Nguyen</u> and John F. Stanton <u>tlam.nguyen@chem.ufl.edu</u>, <u>johnstanton@ufl.edu</u> Quantum Theory Project, Department of Chemistry and Physics, University of Florida, Gainesville, FL 32611 (USA).

Tunneling control of chemical reactions is well known.<sup>1-4</sup> This has been seen for many reactions that involve the motion of hydrogen atoms at low temperature. However, tunneling effects causing a falloff curve (i.e. reaction rate constants depend on pressure) have never been documented to the best of our knowledge. In this work, we provide theoretical evidence that apparently shows tunneling can produce a falloff curve for a reaction that depends on pressure. This is another important feature of quantum tunneling, which is expected to control low temperature chemistry (such as in atmospheric or interstellar environments). In this report, we use high-level coupled-cluster calculations in combination with advanced chemical kinetic techniques to study the reaction OH with HNO<sub>3</sub>, which plays an important role in the upper atmosphere and is fairly well characterized experimentally.<sup>5-6</sup> Our results, in combination with available experimental data, clearly demonstrate that tunneling depends on not only temperature, but also pressure.



1. Schreiner, P. R., Tunneling Control of Chemical Reactions: The Third Reactivity Paradigm (vol 139, pg 15276, 2017). *J Am Chem Soc* **2018**, *140* (4), 1566-1566.

2. Schreiner, P. R.; Reisenauer, H. P.; Ley, D.; Gerbig, D.; Wu, C. H.; Allen, W. D., Methylhydroxycarbene: Tunneling Control of a Chemical Reaction. *Science* **2011**, *332* (6035), 1300-1303.

3. Shannon, R. J.; Blitz, M. A.; Goddard, A.; Heard, D. E., Accelerated chemistry in the reaction between the hydroxyl radical and methanol at interstellar temperatures facilitated by tunnelling. *Nature Chemistry* **2013**, *5* (9), 745-749.

4. Nguyen, T. L.; Xue, B. C.; Weston, R. E.; Barker, J. R.; Stanton, J. F., Reaction of HO with CO: Tunneling Is Indeed Important. *J Phys Chem Lett* **2012**, *3* (11), 1549-1553.

5. Smith, I. W. M., Laboratory studies of atmospheric reactions at low temperatures. *Chem Rev* **2003**, *103* (12), 4549-4564.

6. Brown, S. S.; Talukdar, R. K.; Ravishankara, A. R., Reconsideration of the rate constant for the reaction of hydroxyl radicals with nitric acid. *J Phys Chem A* **1999**, *103* (16), 3031-3037.

## An Experimental and Chemical Kinetic Modeling Study of 1,3-Butadiene Combustion: Ignition delay time and laminar flame speed measurements

Chong-Wen Zhou<sup>a,b</sup>, Yang Li<sup>a</sup>, Ultan Burke<sup>a</sup>, Colin Banyon<sup>a</sup>, Kieran P. Somers<sup>a</sup>, Shuiting Ding<sup>b</sup>, Saadat Khan<sup>c</sup>, Joshua W. Hargis<sup>c</sup>, Travis Sikes<sup>c</sup>, Olivier Mathieu<sup>c</sup>, Eric L. Petersen<sup>c</sup>, Mohammed AlAbbad<sup>d</sup>, Aamir Farooq<sup>d</sup>, Youshun Pan<sup>e</sup>, Yingjia Zhang<sup>e</sup>, Zuohua Huang<sup>e</sup>, Joseph Lopez<sup>f</sup>, Zachary Loparo<sup>f</sup>, Subith S. Vasu<sup>f</sup>, Henry J. Curran<sup>a</sup>

<sup>a</sup>Combustion Chemistry Centre, National University of Ireland Galway, Ireland <sup>b</sup>School of Energy and Power Engineering, Beihang University, Beijing 100191, P. R. China <sup>c</sup>Department of Mechanical Engineering, Texas A&M University, College Station, TX, United States

<sup>d</sup>Clean Combustion Research Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia <sup>e</sup>State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an

710049, People's Republic China

<sup>f</sup>Center for Advanced Turbomachinery and Energy Research (CATER), Mechanical and Aerospace Engineering, University of Central Florida, Orlando, FL, United States

#### Keywords

#### 1,3-butadiene oxidation; shock tube; rapid compression machine; chemical kinetic modeling; flame speed

Ignition delay times for 1,3-butadiene oxidation were measured in five different shock tubes as well as a rapid compression machine (RCM) at thermodynamic conditions relevant to practical combustors. The ignition delay times were measured at equivalence ratios of 0.5, 1.0, and 2.0 in 'air' at pressures of 10, 20 and 40 atm in both the shock tubes and the RCM. Additional measurements were made at equivalence ratios of 0.3, 0.5, 1.0 and 2.0 in argon, at pressures of 1, 2 and 4 atm in a number of different shock tubes. Laminar flame speeds were measured at unburnt temperatures of 295 K, 359 K and 399 K at atmospheric pressure in the equivalence ratio range of 0.6–1.7, and at a pressure of 5 atm at equivalence ratios in the range 0.6–1.4. These experimental data were then used as validation targets for a newly developed detailed chemical kinetic mechanism for 1,3-butadiene oxidation.

A detailed chemical kinetic mechanism (AramcoMech 3.0) has been developed to describe the combustion of 1,3-butadiene and is validated by a comparison of simulation results to the new experimental measurements. Important reaction classes highlighted via sensitivity analyses at different temperatures include: (a) OH radical addition to the double bonds on 1,3-butadiene and their subsequent reactions. The branching ratio for addition to the terminal and central double bonds is important in determining the low-temperature reactivity. (b)  $H\dot{O}_2$  radical addition to the double bonds in 1,3-butadiene and their subsequent reactions. This reaction class is very important in determining the fuel reactivity at low and intermediate temperatures (600–900 K). (c) <sup>3</sup>Ö atom addition to the double bonds in 1,3-butadiene is very important in determining fuel reactivity at intermediate to high temperatures (> 800 K). (d) H atom addition to the double bonds in 1,3-butadiene is very important in the prediction of laminar flame speeds. The formation of ethylene and a vinyl radical promotes reactivity and it is competitive with H-atom abstraction by H atoms from 1,3-butadiene to form the resonantly stabilized C<sub>4</sub>H<sub>5</sub>-i radical and H<sub>2</sub> which inhibits reactivity. Ab initio chemical kinetics calculations were carried out to determine the thermochemistry properties and rate constants for some of the important species and reactions involved in the model development. The present model is a decent first model that captures most of the high-temperature IDTs and flame speeds quite well, but there is room for considerable improvement especially for the lower temperature chemistry before a robust model is developed.

## REACTION BETWEEN PEROXY AND ALKOXY RADICALS CAN FORM STABLE ADDUCTS

Matti P. Rissanen<sup>1, 2\*</sup>, Siddharth Iyer<sup>3</sup> and Theo Kurtén<sup>3</sup>

 <sup>1</sup>Aerosol Physics Laboratory, Physics Unit, Tampere University, FI-33101 Tampere, Finland
 <sup>2</sup>Department of Physics and Institute for Atmospheric and Earth System Research (INAR), University of Helsinki, FI-00014 Helsinki, Finland
 <sup>3</sup>Department of Chemistry and Institute for Atmospheric and Earth System Research (INAR), University of Helsinki, FI-00014 Helsinki, Finland

#### Keywords

Alkoxy radicals, Peroxy radicals, Atmospheric oxidation, Secondary organic aerosol, Organic oxidized dimers.

Gas-phase oxidation of *volatile organic compounds* (VOCs) is mediated by *alkoxy* (RO) and *peroxy* (RO<sub>2</sub>) radical intermediates. While the peroxy radicals are generally relatively unreactive free radicals reacting appreciably only with other peroxy radicals (RO<sub>2</sub> and HO<sub>2</sub>) and NO<sub>x</sub> (=NO and NO<sub>2</sub>), the alkoxy radical intermediates are often highly reactive with O<sub>2</sub> and possess facile unimolecular dissociation channels (Orlando and Tyndall, 2012). Recently, the formation of oxidized organic "dimer" compounds has attracted considerable attention due to their potentially crucial role in seeding atmospheric nanoparticles, yet their formation pathways have remained elusive (Kurtén, et al., 2016; Kirkby et al., 2016; Rissanen MP 2018). Here we report a hitherto unrecognized gas-phase pathway of oxidative molecular growth by RO<sub>2</sub> + R'O forming "stable" trioxides and leading to matching molecular compositions to previously assigned dimer compounds (Iyer et al., 2019).

Computational methods were used to study the mechanism and kinetics of the prototypical  $R'O_2 + RO$  reactions of alkyl, acyl and  $\beta$ -oxo peroxy and alkoxy radicals. On the singlet surface, R'OOOR adducts are rapidly formed. For selected combinations of R'O and  $RO_2$ , the trioxides were found to be stable enough to likely contribute to atmospheric new particle formation and growth, and we conservatively estimated the ambient steady-state concentrations of R'OOOR to reach even a value of  $3 \times 10^4$  molecules cm<sup>-3</sup>. This finding has potentially important consequences on understanding organic aerosol formation in highly-polluted megacities, were frequent new particle formation events have been observed despite the large condensation sink present from pre-existing airborne particulates (Yu et al., 2016; Yao et al., 2018).

#### References

Iyer S, Rissanen MP, Kurtén T. Reaction between Peroxy and Alkoxy Radicals Can Form Stable Adducts. J Phys Chem Lett 2019;10:2051-2057.

Kirkby J et al. Ion-induced nucleation of pure biogenic particles. Nature 2016;533:521-526.

Kurtén T, Tiusanen K, Roldin P, Rissanen M, Luy JN, Boy M, Ehn M, Donahue N. α-Pinene Autoxidation Products May Not Have Extremely Low Saturation Vapor Pressures Despite High O:C Ratios. J Phys Chem A 2016;120:2569-2582.

Orlando JJ, Tyndall GS. Laboratory studies of organic peroxy radical chemistry: an overview with emphasis on recent issues of atmospheric significance. Chem Soc Rev 2012;41:6294-6317.

Rissanen MP. NO2 Suppression of Autoxidation–Inhibition of Gas-Phase Highly Oxidized Dimer Product Formation, ACS Earth and Space Chem 2018;2:1211-1219.

Yao L et al., Atmospheric new particle formation from sulfuric acid and amines in a Chinese megacity. Science 2018;361:278-281.

Yu H, Zhou L, Dai L, Shen W, Dai W, Zheng J, Ma Y, Chen M, Nucleation and growth of sub-3 nm particles in the polluted urban atmosphere of a megacity in China. Atmos Chem Phys 2016;16:2641-2657.

\*Corresponding author: matti.rissanen@tuni.fi

### Group additive kinetic modeling for the pyrolysis of cyclic species

Florence H. Vermeire<sup>1</sup>, Ruben Van de Vijver<sup>1</sup> Guy B. Marin<sup>1</sup> and Kevin M. Van Geem<sup>1,\*</sup> <sup>1</sup>Laboratory for Chemical Technology, Ghent University, Technologiepark 125, 9052 Gent, Belgium

Keywords

Group additive values, Cyclic species, Soot formation

The automatic kinetic model generation software Genesys (Vandewiele et al. 2012) has successfully been applied to produce accurate kinetic models for the pyrolysis and oxidation of hydrocarbons and hetero-atomic components. The fast determination of kinetic parameters is crucial in automatic kinetic model generation, for which Genesys uses the group additive methodology developed by Willems and Froment and extended by Sabbe et al. (Sabbe et al. 2008). This method determines the activation energy and pre-exponential factor of a reaction based on the differences in the reactive center relative to a reference reaction. The accuracy of the resulting kinetics depends on the availability of group additive values. For reactions that involve cyclic species, current databases are lacking.

To allow the automatic generation of kinetic models for processes such as soot formation or the pyrolysis and combustion of cyclic species from bio-based feedstocks, we have focused on extending the current group additive databases to include cyclic hydrocarbons. Three reaction families have been considered: the formation of C<sub>6</sub> rings through intramolecular and intermolecular Diels Alder cyclization reactions, formation of C<sub>5</sub> and C<sub>6</sub> rings through intramolecular radical addition reactions, and hydrogen shift reactions in C<sub>5</sub> and C<sub>6</sub> rings. An example of an intramolecular Diels Alder reaction and the application of group additive values to determine kinetics is given in Figure 1. The mean absolute error on the resulting rate coefficient is within a factor of 3 of the CBS-QB3 ab initio rate coefficient.



Figure 1. Intramolecular Diels Alder reaction, assignment of reactive centra and calculation of the pre-exponential factor and activation energy relative to the reference reaction

#### References

Sabbe, M. K., M. F. Reyniers, V. Van Speybroeck, M. Waroquier, and G. B. Marin. 2008. 'Carbon-centered radical addition and beta-scission reactions: Modeling of activation energies and pre-exponential factors', *Chemphyschem*, 9: 124-40.

Vandewiele, N. M., K. M. Van Geem, M. F. Reyniers, and G. B. Marin. 2012. 'Genesys: Kinetic model construction using chemo-informatics', *Chemical Engineering Journal*, 207-208: 526-38.

## PRESSURE DEPENDENT KINETICS OF THE REACTION BETWEEN CH<sub>3</sub>O<sub>2</sub> and OH: TRIOX FORMATION

<u>Chao Yan</u><sup>1,2</sup> and Lev N. Krasnoperov<sup>2,\*</sup> <sup>1</sup> Princeton University, Princeton, NJ, 08540, U.S.A <sup>2</sup> New Jersey Institute of Technology, Newark, NJ, 07102, U.S.A

Keywords

Branching ratios, High pressure, Kinetics, Methyl peroxy radical, Triox Formation.

Methyl peroxy radical,  $CH_3O_2$ , plays an important role as a reaction intermediate in the lowtemperature combustion as well as atmospheric oxidation of hydrocarbons. One of the potential important channels for the reaction of methyl peroxy radicals ( $CH_3O_2$ ) with hydroxyl radicals (OH) is production of methylhydrotrioxide  $CH_3OOOH$  (TRIOX) (Muller et al., 2018):

$CH_3O_2$	+	OH	$\rightarrow$	CH <sub>3</sub> O	+	$HO_2$	(1a)
			$\rightarrow$	$^{3}CH_{2}OO$	+	$H_2O$	(1b)
			$\rightarrow$	CH <sub>3</sub> OOOH			(1c)
			$\rightarrow$	CH <sub>3</sub> OH	+	$O_2$	(1d)

In this work, pressure dependence of the yield of  $HO_2$  radicals in channel 1a was studied at ambient temperature over the 1-100 bar pressure range. The radicals were produced by photolysis  $N_2O/H_2O/(CH_3)_2CO/O_2/He$  mixtures at 193 nm. Transient absorption profiles of OH,  $CH_3O_2$  and  $HO_2$  were recorded in the UV region. Transient absorption profiles of HO<sub>2</sub> at 210 nm and 224 nm were used to determine the branching ratio of channel 1a. Pressure "quenching" of  $HO_2$  yield (channel 1a) was observed (Figure 1, black solid line). Assuming the only channels 1a and 1c play role, the yield of TRIOX is determined (Figure 1, black dotted line). The results indicate that



TRIOX formation and subsequent reactions could be important in combustion at high pressures (such as in internal combustion engines, etc.) as well as at ambient pressure at low temperatures.

#### References

Müller, J.-F. et al. The Reaction of Methyl Peroxy and Hydroxyl Radicals as a Major Source of Atmospheric Methanol. *Nature Communications* 2016: 7: 13213.

\*Corresponding author: lev.n.krasnoperov@njit.edu

## THE CRIEGEE INTERMEDIATE REACTION NETWORK IN ETHYLENE OZONOLYSIS

Nils Hansen<sup>1,\*</sup>, Aric C. Rousso<sup>2</sup>, Ahren W. Jasper<sup>3</sup> and Yiguang Ju<sup>2</sup> <sup>1</sup>Combustion Research Facility, Sandia National Laboratories, Livermore, CA 945501, USA <sup>2</sup>Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey 08544, USA <sup>3</sup>Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois 60439, USA

Keywords

Ozonolysis, Criegee intermediate, jet-stirred reactor, molecular-beam mass spectrometry

Ethylene ozonolysis at atmospheric pressure was studied from 300-1000 K in a jet-stirred reactor using molecular-beam mass spectrometry. The identification and quantification of previously elusive intermediates were carried out by combining experimentally observed photoionization efficiency curves with *ab initio* calculations for isomer-specific ionization threshold. Many previously elusive hydroperoxide species, including the keto-hydroperoxide HOOCH<sub>2</sub>CHO (hydroperoxyl-acetaldehyde), were identified. Temperature-dependent mole fractions are reported that can serve as validation targets for future model development. The network of reactions of the Criegee Intermediate was explored and evidence for up to four sequential CI additions were found, resulting in highly oxygenated species.

This contribution is largely based on recent publications (Rousso et al., 2018 and Rousso et al., 2019).

#### References

Rousso AC, Hansen N, Jasper AW, Ju Y. Identification of the Criegee Intermediate Reaction Network in Ethylene Ozonolysis: Impact on Energy Conversion Strategies and Atmospheric Chemistry. Phys Chem Chem Phys 2019;21:7341-7357

Rousso AC, Hansen N, Jasper AW, Ju Y. Low-Temperature of Ethylene by Ozone in a Jet-Stirred Reactor. J Phys Chem A 2018;122:8674-8685

## Pressure dependent kinetics of the reaction between CH<sub>3</sub>O<sub>2</sub> and OH focusing on the product yield of methyltrioxide (CH<sub>3</sub>OOOH)

Feng Zhang<sup>1</sup>, Can Huang<sup>1,2</sup>

<sup>1</sup> National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui, 230029, P. R. China

<sup>2</sup> Center for Combustion Energy and Key Laboratory for Thermal Science and Power Engineering of MOE, Tsinghua University, Beijing, 100084, P. R. China

Keywords

Peroxy radicals; hydroxyl radical; methyltroxide; atmospheric chemistry; RRKM/master equation

There is an ongoing debate on whether the reaction between methyl peroxy radical (CH<sub>3</sub>OO) and hydroxyl radical (OH) acts as a source of atmospheric methanol (Muller et al. 2016; Caravan et al. 2018; Ferracci et al., 2018). The central focus of the debate rests on the branching yield of stabilized methyltrioxide (CH<sub>3</sub>OOOH, TRIOX). The large branching yield leads to a positive conclusion, whereas the small value does not. Here we revisit this interesting problem by systematically investigating the pressure dependent kinetics of the reaction through combined coupled cluster and RRKM/master equation methods. Our calculated branching ratio of TRIOX is quite small, around 0.04 at 298 K, 760 Torr, in consistent with the latest experimental result. It is shown that the large branching yield obtained in an early study is mainly originated from the collision induced strong stabilization presented in their simulation. Our findings highlight the importance of pressure dependent kinetics in correctly understanding radical reactions in general.

#### References

Muller JF, Liu Z, Nguyen VS, Stavrakou T, Harvey JN, Peeters J. The reaction of methyl peroxy and hydroxyl radicals as a major source of atmospheric methanol. Nature Comm. 2016; 7:13213.

Caravan RL, Khan MAH, Zádor J. Sheps L, Antonov IO, Rotavera B, Ramasesha K, Au K, Chen MW, Rösch D, Osborn DL, Fittschen C, Schoemaecker C, Duncianu M, Grira A, Dusanter S, Tomas A, Percival CJ, Shallcross DE, Taatjes CA. The reaction of hydroxyl and methylperoxy radicals is not a major source of atmospheric methanol. Nature Comm. 2018; 9: 4343.

Ferracci V, Heimann I, Abraham NL, Pyle JA, Archibald AT. Global modelling of the total OH reactivity: investigations on the "missing" OH sink and its atmospheric implications. Atmos. Chem. Phys. 2018, 18, 7109-7129.

## Modeling PAH formation using RMG: From acetylene to three rings

Mengjie Liu, Te-Chun Chu, Agnes Jocher, Mica C. Smith, and William H. Green<sup>\*</sup> Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

Keywords

Polycyclic aromatic hydrocarbons, Reaction Mechanism Generator, pyrolysis, modeling, automatic

Understanding the formation of polycyclic aromatic hydrocarbons (PAHs) is of particular interest due to their harmful effects on human health (Kim et al., 2013). PAH formation is also highly undesirable in chemical and fuel production, since they tend to condense as tar, coke, or other deposits causing operational problems. Detailed chemical mechanisms can help us identify the most important pathways leading to PAH formation, which may be helpful in avoiding their formation. To construct such mechanisms, we use the Reaction Mechanism Generator (RMG), an open-source software package developed in our group (Gao et al., 2016). RMG was recently used to model PAH formation in methane-rich oxidation to great success (Chu et al., 2019). However, there are still many challenges remaining in robustly generating models going beyond two aromatic rings.

In this work, we present efforts towards improving RMG's ability to model formation of larger PAHs. The focus of this work is on improving the rate and thermochemical parameters used by RMG, and ensuring that RMG is able to generate potentially relevant pathways which have been previously studied in literature. Among these, we highlight the HACA, naphthyl + vinylacetylene, and benzyne addition pathways, with considerations for pressure dependent rate coefficients evaluated using Arkane. With these additions to the RMG-database, we generated a model for acetylene pyrolysis and present our results in comparison to experimental data from literature. Remaining challenges in this branch of chemical kinetics will be briefly discussed.

#### References

Chu, T.-C.; Buras, Z. J.; Oßwald, P.; Liu, M.; Goldman, M. J.; Green, W. H. Modeling of aromatics formation in fuel-rich methane oxy-combustion with an automatically generated pressure-dependent mechanism. *Phys. Chem. Chem. Phys.* **2019**, *21* (2), 813–832.

Gao, C. W.; Allen, J. W.; Green, W. H.; West, R. H. Reaction Mechanism Generator: Automatic construction of chemical kinetic mechanisms. *Comput. Phys. Commun.* **2016**, *203*, 212–225.

Kim, K.-H.; Jahan, S. A.; Kabir, E.; Brown, R. J. C. A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects. *Environ. Int.* **2013**, *60*, 71–80.

## Reaction Products of Fuel Derived CH Radical Reactions with Ammonia and Substituted Amines by Using SVUV Photoionization Coupled to Time-of-Flight Mass Spectrometry

Jérémy Bourgalais<sup>1</sup>, Kacee Caster<sup>2</sup>, Olivier Durif<sup>3</sup>, David Osborn<sup>4</sup>, Sébastien Le Picard<sup>3</sup>, Fabien Goulay<sup>2</sup>

<sup>1</sup>LATMOS/IPSL, UVSQ Université Paris-Saclay, Sorbonne Université, CNRS, Guyancourt, France

2Combustion Research Facility, Mail Stop 9055, Sandia National Laboratories, Livermore, California 94551, United States

3Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506, United States

4Institut de Physique de Rennes, Département de Physique Moléculaire, Astrophysique de Laboratoire, UMR CNRS 6251, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

#### Keywords

#### Combustion - Synchrotron Radiation - Mass Spectrometry - Isomers - Branching Ratios

Biofuels containing oxygenated and nitrogenized speciesare used as additives and substitutes for usual fossil fuels. However, regarding the fuel structure biofuel combustion could contribute to the formation of reactive harmful nitrogenized pollutants. Ammonia and its amine derivatives are emitted as gases in the atmosphere from a variety of sources and are therefore of special interest in combustion environments. Accordingly, an improved utilization of biomass-derived nitrogen-containing compounds as fuels and a better understanding of the role of amines in combustion both require a systematic study of the chemistry of ammonia and substituted amines with combustion relevant radicals.

We investigated the reactions of the methylidyne radical with ammonia and substituted amines under multiple collision conditions at relatively low pressure (4 torr) and room temperature. We identified reaction products by using synchrotron VUV photoionization coupled to time-of-flight mass spectrometry (TOF-MS) at the Advanced Light Source (ALS-CA/USA) synchrotron. Kinetic traces of the species were used to discriminate between primary and secondary products.

The reaction of the CH radical with ammonia is found to form mainly imine, in line with an addition-elimination mechanism. The singly methyl-substituted imine is detected for the CH reactions with methylamine, dimethylamine, and trimethylamine. Dimethylimine isomers are formed by the reaction of CH with dimethylamine, while trimethylimine is formed by the CH reaction with trimethylamine. In the case of the reactions with methylamine and dimethylamine, product formation is assigned to an addition-elimination mechanism similar to that proposed for the CH reaction with ammonia. However, this mechanism cannot explain the products detected by the reaction with trimethylamine and another insertion pathway may become more probable as the number of methyl groups increases.

## Direct measurements of PAH formation and growth by addition of phenyl and naphthyl radicals to acetylene

Mica C. Smith<sup>1</sup>, Te-Chun Chu,<sup>1</sup> Jeehyun Yang,<sup>1</sup> Awele Uwagwu,<sup>1</sup> Mengjie Liu,<sup>1</sup> and William H. Green<sup>1\*</sup> <sup>1</sup>Massachusetts Institute of Technology, Cambridge, MA, USA

Keywords

Polycyclic aromatic hydrocarbons, HACA, soot, photoionization mass spectrometry, radicals

Polycyclic aromatic hydrocarbons (PAHs) are byproducts of combustion which contribute to environmental pollution and endanger human health (Abdel-Shafy and Mansour, 2016). Chemical routes to PAHs in the gas phase and their subsequent transition into the particle phase remain elusive. The most famous proposed reaction pathway, called hydrogen-abstraction-acetylene-addition (HACA), involves acetylene addition to aromatic radicals, and is generally accepted as a primary contributor to the formation of PAHs and soot (Bockhorn, 2013). These addition reactions have been explored by theoretical methods, but few experimental investigations exist to assess the validity of calculated rates and branching ratios.

We investigated the reactions of phenyl and naphthyl radicals with acetylene using VUV photoionization time-of-flight mass spectrometry at temperatures from 500 to 800 K in the Combustion Dynamics Laboratory at MIT (Middaugh et al., 2018). For phenyl + acetylene, products corresponding to phenylacetylene, naphthalene, and  $C_8H_7$  radicals were observed, and naphthalene was found to be the dominant product under all conditions. Branching ratios for the chemically activated channels of naphthalene and phenylacetylene formation are presented. In the 1-naphthyl + acetylene reaction,  $C_{12}H_9$  radicals and  $C_{12}H_8$  were observed, indicating the formation of acenaphthalene via acetylene addition, while for 2-naphthyl + acetylene, we observed both  $C_{12}H_8$  and  $C_{14}H_{10}$  PAH products in addition to  $C_{12}H_9$  radical intermediates. The appearance of  $C_{14}H_{10}$  is the first direct, intermediate-resolved experimental evidence for a HACA pathway from naphthalene to phenanthrene and anthracene.

#### References

Abdel-Shafy HI, Mansour MSM. A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. Egypt. J. Petrol. 2016;25:107-123.

Bockhorn H. Soot Formation in Combustion: Mechanisms and Models. Berlin: Springer-Verlag; 2013. 168-175.

Middaugh JE, Buras ZJ, Matrat M, Chu TC, Kin YS, Alecu IM, Vasiliou AK, Goldsmith CF, Green WH. A combined photoionization time-of-flight mass spectrometry and laser absorption spectrometry flash photolysis apparatus for simultaneous determination of reaction rates and product branching. Rev Sci Instrum 2018;89:074102.

## **REACTION OH + OH** $\rightarrow$ H<sub>2</sub>O + O REVISITED

Xiaokai Zhang<sup>1</sup>, Manuvesh Sangwan<sup>1</sup>, Chao Yan<sup>1</sup>, Pavel V. Koshlyakov<sup>2</sup>, Evgeni N. Chesnokov<sup>2</sup>

and <u>Lev N. Krasnoperov<sup>1,\*</sup></u>

<sup>1</sup>New Jersey Institute of Technology, Newark, NJ, 07102, U.S.A

<sup>2</sup>Institute of Chemical Kinetics and Combustion, Novosibirsk, 630090, Russia

#### Keywords

Kinetics, Hydroxyl Radical, Self-Reaction, Disproportionation.

The kinetics of the disproportionation channel 1a of the self-reaction of hydroxyl radicals remains controversial over the past two decades:  $OH + OH \rightarrow H_2O + O$  (1a). The room temperature  $k_{1a} = 1.48 \times 10^{-12}$  cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup> as well as the negative temperature dependence at moderate temperatures obtained using discharge flow system (Bedjanian et al., 1999) are currently accepted in the IUPAC recommendations. Then reaction was re-measured using pulsed photolysis N<sub>2</sub>O/H<sub>2</sub>O mixtures at 193 nm yielding factor ca. 1.8 higher value of  $2.7 \times 10^{-12}$ cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup> (Bahng and Mcdonald, 2007). Kinetics of the title reaction was then investigated using photolysis N<sub>2</sub>O/H<sub>2</sub>O/O<sub>2</sub> at 193 nm at high pressures by monitoring ozone formed from oxygen atoms produced in channel 1a (Sangwan and Krasnoperov, 2012). The low value of  $k_{1a}$  was confirmed, as well as the turning point in the temperature dependence of  $k_{1a}$  at ca. 500 K was reported. Subsequently, the reaction was re-measured using essentially the same approach (Altinay and Macdonald, 2014) yielding again the high value of  $k_{1a}$  and confirming the turning point in the temperature dependence at ca. 500 K.

In this work, the kinetics of the title reaction was investigated using two different techniques to produce  $O(^{1}D)$  atoms which subsequently produce OH radical via fast reaction with H<sub>2</sub>O. The photolysis of ozone at 266 nm (4<sup>th</sup> harmonic of Nd:YAG laser) as well as photolysis of N<sub>2</sub>O at 193 nm (ArF excimer laser) were used. In addition, experiments with direct photolysis of water have been performed. The experiments consistently resulted in the low rate constant,  $k_{1a} = (1.4 \pm 0.2) \times 10^{-12} \text{ cm}^{3}$ molecule<sup>-1</sup>s<sup>-1</sup>. Possible problems with the hydroxyl radical generation at high [N<sub>2</sub>O]/[H<sub>2</sub>O] ratios are discussed.

#### References

Altinay, G.; Macdonald, R.G. Determination of the Rate Constant for the  $OH(X^2\Pi) + OH(X^2) \rightarrow H_2O + O(^{3}P)$  Reaction Over the Temperature Range 295 to 701 K. J. Phys. Chem. A, 2014;118: 38–54.

Bahng, M.-K.; Macdonald, R.G. Determination of the Rate Constant for the OH( $X^2\Pi$ ) + OH( $X^2\Pi$ )  $\rightarrow$  O(<sup>3</sup>P) + H<sup>2</sup>O Reaction over the Temperature Range 293–373 K. J. Phys. Chem. A, 2007;111:3850-3861.

Bedjanian, Y.; Le Bras, G.; Poulet, G. J. Kinetics of Self Reaction of OH Radicals, J. Phys. Chem. A, 1999;103:7017-7025.

Sangwan, M.; Krasnoperov, L.N. Disproportionation Channel of Self-Reaction of Hydroxyl Radical,  $OH + OH \rightarrow H_2O + O$ , Studied by Time-Resolved Oxygen Atom Trapping. *J. Phys. Chem. A*, 2012;116:11817–11822.

\*Corresponding author: lev.n.krasnoperov@njit.edu

## REACTIVITY COMPARISON OF LINEAR C<sub>4</sub>-C<sub>6</sub> ALCOHOL, ALDEHYDE AND CARBOXYLIC ACID OXIDATION.

Sylvain Namysl<sup>1</sup>, Matteo Pelucchi<sup>2</sup>, Olivier Herbinet<sup>1</sup>, Tiziano Faravelli<sup>2</sup> and Frederique Battin-Leclerc<sup>1,\*</sup>

<sup>1</sup>LRGP, CNRS-Université de Lorraine, 1 rue Grandville, 54000 Nancy, FRANCE <sup>2</sup> Department of Chemistry, Materials and Chemical Engineering "G. Natta ", Politecnico di Milano, P.zza Leonardo da Vinci 32, 20133 Milano, ITALY

#### Keywords: Oxygenated fuels, oxidation, jet-stirred reactor

The use of fuels obtained from the transformation of biomass, such as biogas and bio-oil, is becoming more and more important in combustion processes. However due to the mixture complexity, their gas-phase oxidation chemistry (reactivity, pollutants formation...) is still not well known despite the latest studies performed and therefore surrogates have to be defined and studied. In the case of bio-oils, linear oxygenated molecules can be suitable surrogate components, as they represent a non-negligible part of their compositions.

This work compares the results from recent studies carried out on three different types of linear oxygenated compounds: alcohols, aldehydes and carboxylic acids. For each type of functional group, the studied fuels contained between 4, 5 and 6 carbon atoms. Table 1 presents the studied fuels.

	Alcohol	Aldeh	iyde	Carboxylic Acid		
4 carbon atoms	он	~~~ <sub>0</sub>	Pelucchi et al (2019)	ОН	Namysl et al (2019)	
5 carbon atoms	ОН		Pelucchi et al (2019)	ОН	Namysl et al (2019)	
6 carbon atoms	ОН		Rodriguez et al (2012)	-		

Table 1. Fuels studied in this work sorted along their carbon atom number and their oxygenated function.

The oxidation of these 8 fuels was studied in a jet-stirred reactor between 500 K and 1100K at atmospheric pressure. For each fuel, three equivalence ratios have been investigated: fuel-lean (0.5), stoichiometric (1) and fuel-rich (2) conditions. Thanks to gas chromatography coupled with different detectors and mass spectrometry, mole fraction profiles have been obtained and compared to results obtained with the CRECK kinetic model.

The 8 fuels with 3 different oxygenated functions are compared according to different criteria: bond dissociation energies and the effect of the oxygenated function on the product distribution and on fuel reactivity. The final objective of this work is to propose new rate rules for linear oxygenated compounds such as those already used for alkanes.

#### References

Namysl S, Pelucchi M, Herbinet O, et al. A first evaluation of butanoic and pentanoic acid oxidation kinetics. Chem. Eng. J. Submitted; 2019.

Pelucchi M, Namysl S, Ranzi E, et al. An experimental and kinetic modeling study of  $n-C_4-C_6$  aldehydes oxidation in a jet-stirred reactor. Proc. Combust. Inst. 2019; 37: 389-397.

Rodriguez A, Herbinet O and Battin-Leclerc F. A study of the low-temperature oxidation of a long chain aldehyde: n-hexanal. Proc. Combust. Inst. 2017; 36: 365–372.

This work has received funding from the European Union H2020 (H2020-SPIRE-04-2016) under grant agreement n°723706 and from the COST Action CM1404 "Chemistry of smart energy carriers and technologies".

## A GAS-PHASE REACTION MODEL FOR SI-CVD SIMULATION UNDER ATMOSPHERIC OR MODERATE PRESSURE

Kaito Noda<sup>1,2, \*</sup>, Nilson Kunioshi<sup>1</sup>, Yoshihiro Jagawa<sup>2</sup> and Akio Fuwa<sup>3</sup> <sup>1</sup>Graduate School of Fundamental Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, JAPAN <sup>2</sup>SUMCO Corporation, 1-52 Kubara, Yamashiro-cho, Imari-shi, Saga 849-4256, JAPAN <sup>3</sup>Professor Emeritus, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, JAPAN

#### Keywords

Chemical vapor deposition, Reaction analysis, Unimolecular reactions, Pressure dependence, Gas-phase reaction

In the reaction analysis of silicon CVD epitaxial growth using SiHCl<sub>3</sub> as the source gas, many of the rate coefficients for the elementary reactions in the gas-phase available in the literature are in the high pressure limit, and their pressure dependence have not been clarified yet. Under atmospheric or moderate pressure conditions, it may be necessary to use rate coefficients whose pressure dependence is considered, because this enables a more precise analysis of the reactions in silicon CVD process.

In this work, we built a reaction model that can be used to simulate the gas-phase reactions occurring in silicon CVD reactors under atmospheric or moderate pressure. The rate coefficients of unimolecular reactions and related chemical activated reactions that were included in an existing reaction model used in the past to simulate SiCl<sub>4</sub> clean conversion into SiHCl<sub>3</sub> (Kunioshi et al, 2016) were calculated as a function of pressure and temperature based on ab initio molecular orbital theory and RRKM theory. The stationary points in the potential energy surface were optimized and their vibrational frequencies and rotational constants calculated at the (U)B3LYP/6–31+G(d,p) level of theory; the CCSD(T)/aug-cc-pVTZ level was then used for accurate estimation of activation energies. The master equation was solved using SSUMES. The reactions analyzed here occurred among the 12 species listed in Table 1, and the applicability of the newly calculated rate coefficients in the reaction model was discussed. The results showed that the reactions investigated are in the fall-off regime under atmospheric or moderate pressure conditions, and suggest that accurate modeling of silicon CVD processes requires careful determination of the rate coefficients as functions of pressure and temperature for the conditions of interest.

Table 1. The species analyzed their unimolecular reactions and related chemical activated reaction.SpeciesSiHCl<sub>3</sub>, SiH<sub>2</sub>Cl<sub>2</sub>, SiH<sub>3</sub>Cl, SiCl<sub>4</sub>, SiH<sub>3</sub>, SiCl<sub>3</sub>, Cl<sub>3</sub>SiSiH<sub>2</sub>Cl, HCl<sub>2</sub>SiSiHCl<sub>2</sub>, Si<sub>2</sub>HCl<sub>5</sub>,<br/>Si<sub>2</sub>Cl<sub>6</sub>, Cl<sub>3</sub>SiSiCl, Cl<sub>2</sub>SiSiCl<sub>2</sub>

#### References

Kunioshi N, Moriyama Y, Fuwa A. Kinetics of the Conversion of Silicon Tetrachloride into Trichlorosilane Obtained through the Temperature Control along a Plug-Flow Reactor. Int J Chem Kinet 2016;48:45-57.

\*Correspondence to: Kaito Noda; e-mail: kaito@suou.waseda.jp.

## DETAILED EXPERIMENTAL AND KINETIC MODELING STUDY OF 3-CARENE PYROLYSIS

Jia Zhang<sup>1</sup>, Florence Vermeire<sup>1</sup>, Ruben Van de Vijver<sup>1</sup>, Olivier Herbinet<sup>2</sup>, Frédérique Battin-Leclerc<sup>2</sup>, Marie-Françoise Reyniers<sup>1</sup> and Kevin M. Van Geem<sup>1,\*</sup> <sup>1</sup>Laboratory for Chemical Technology, Ghent University, Gent, Belgium <sup>2</sup>Laboratoire Réactions et Génie des Procédés, CNRS, Université de Lorraine, Nancy, France

#### Keywords

3-carene, jet-stirred reactor, automatic kinetic model generation, potential energy surface, aromatics formation

3-carene is an important potential biofuel with properties similar to the jet-propellant JP-10. Its thermal decomposition and combustion behavior is to date unknown, which is essential to assess its quality as a fuel. A combined experimental and kinetic modelling has been conducted to understand the 3-carene pyrolysis chemistry. The pyrolysis of 3-carene was investigated in a jet stirred quartz reactor at atmospheric pressure. Details on the experimental unit can be found elsewhere (Herbinet and Battin-Leclerc 2014). The experimental temperature is varied from 650K to 1050K and the average residence time about 2 seconds. The effluent is mainly composed of C<sub>5-</sub> molecules and a variety of aromatic species, all detected by online gas chromatography. The initial decomposition pathways of 3-carene were identified using the KinBot software. There is a direct Diels-Alder pathway which forms isoprene and 3,3-diemethyl-cyclopropane. The hydrogen gas elimination reaction has the lowest reaction energy barrier. Other pathways are the ring opening reactions of the three-membered ring which generate intermediates for aromatics formation. The primary decomposition chemistry of 3-carene is calculated from quantum mechanical calculations at the CBS-QB3 level of theory. The resulting rate coefficients and thermodynamic properties are used in an elementary 3-carene pyrolysis kinetic model that is automatically generated by Genesys (Vandewiele, Van Geem et al. 2012).



Figure 1: The Potential Energy Surface for initial decomposition of 3-carene (Left), Mole fractions of 3-carene, isoprene, terpinolene and p-cymene (Right)

#### References

Herbinet, O. and F. Battin-Leclerc (2014). International Journal of Chemical Kinetics 46(10): 619-639.

Vandewiele, N. M., K. M. Van Geem, M.-F. Reyniers and G. B. Marin (2012). Chemical Engineering Journal 207–208(0): 526-538.

\*Corresponding author: Kevin.VanGeem@UGent.be

# Coupling between gas-phase and surface chemistry in catalytic combustion

Katrin Blondal<sup>1</sup>, Jelena Jelic<sup>2</sup>, Emily Mazeau<sup>3</sup>, Felix Studt<sup>2</sup>, Richard H. West<sup>3</sup> and C. Franklin Goldsmith \*1

<sup>1</sup>School of Engineering, Brown University, Providence, RI, USA
<sup>2</sup>Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology,76344
Eggenstein-Leopoldshafen, GERMANY
<sup>3</sup>Department of Chemical Engineering, Northeastern University, Boston, MA 02115, USA

Keywords

catalytic combustion, platinum, automatic mechanism generation, DFT, homogeneous/heterogeneous coupling

This talk summarizes recent efforts to expand the functionality of the software package RMG-CAT, which automatically generates microkinetic mechanisms in heterogeneous catalysis. RMG-CAT has been expanded significantly. First, the thermodynamic database now contains 69 new adsorbates for the  $H_aC_bN_cO_d$  system on platinum, with the electronic structure properties were computed using the BEEF-vdW functional. Second, RMG-CAT now can access all the gas-phase chemistry inherent in RMG, which allows for seamless integration of surface- and gas-phase chemistry in a thermodynamically consistent manner. RMG-CAT is tested on the catalytic combustion of methane on platinum. The modeling results reveal that under some conditions, such as when the residence time in the catalytic zone of a plug-flow reactor is too short, the catalytic surface can induce gas-phase light-off. Modeling results reveal that this light-off is largely due to the desorption of hydroxyl radicals into the gas phase.



\*Corresponding author: franklin\_goldsmith@brown.edu

## A Theoretical and Kinetic Analysis of Phenol Pyrolysis

Luna Pratali Maffei<sup>1,\*</sup>, Matteo Pelucchi<sup>1</sup>, Tiziano Faravelli<sup>1</sup> and Carlo Cavallotti<sup>1</sup>

<sup>1</sup>CRECK Modeling Lab, Department of Chemistry Materials and Chemical Engineering, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133, Milan, ITALY

#### Keywords

#### Phenol, Combustion, Kinetic modeling, Oxygenated aromatics, Ab initio, Master Equation

Understanding quantitatively the reaction kinetics of oxygenated aromatics is of key relevance in order to be able to model properly the reactivity of biofuels. Oxygenated aromatics are in fact among the main components of the bio-oils derived from the fast-pyrolysis of biomass (Faravelli et al., 2010). With the intent of developing an accurate and detailed understanding of the reaction kinetics of aromatics and with the final goal of determining rate rules, in this work we theoretically investigate the key reactions in the pyrolysis of phenol. Phenol can be considered as a reference compound for the pyrolysis mechanism of other substituted phenolic species such as anisole, guaiacol, catechol, and vanillin, often present in bio-oils, and is a key intermediate in benzene oxidation. A preliminary kinetic analysis of phenol pyrolysis performed using the POLIMI 1905 mechanism showed that the most sensitive reactions, neglecting those for which well assessed parameters are available, are phenol and phenoxy decomposition, and H-abstraction by H from phenol and cyclopentadiene ( $cC_5H_6$ ). We therefore computed rate constants for all the identified decomposition and abstraction reactions using ab initio transition state theory based (TST) master equation calculations. Stationary points on the Potential Energy Surface (PES) were determined at the wB97XD (decomposition) and M06-2X (abstraction) level using large basis sets, while energies were computed at the CCSD(T) level, with extension to the complete basis set limit. Notably, and despite the small T1 diagnostic, it was found that phenol decomposition to  $cC_5H_6$  and CO, one of its main reaction channels, has a significant multireference character. Energy barriers and geometric structures for this reaction were therefore determined at the CASPT2 level using active spaces up to (12e,11o) and basis sets up to aug-ccpVTZ. The CASPT2 energy is about 4 kcal/mol smaller than that determined at the CCSD(T) level. Rate constants of barrierless decomposition channels were determined using variational TST on CASPT2 PESs. All calculations were performed using the EStokTP software (Cavallotti et al., 2019), with pressure dependent rate constant evaluated using MESS (Georgievskii et al., 2013). The present calculations were performed at a level of theory higher for accuracy in energy determination and rate constant calculations than presently available in the literature.

The theoretically determined rate constants were then inserted in the POLIMI 1905 mechanism and used to simulate the available literature PFR and Shock Tube data on phenol pyrolysis. The agreement with experimental data is good for what concerns phenol conversion and cyclopentadiene and atomic hydrogen formation. Some discrepancies with experimental evidences suggest that literature cyclopentadiene decomposition rates need to be revised.

#### References

Faravelli T, Frassoldati A, Migliavacca A, Ranzi E. Biomass and Bioenergy 2010;34(3):290-301 Cavallotti C, Pelucchi M, Georgievskii Y, Klippenstein S. J. J. Chem. Theory Comput. 2019;15:1122

Georgievskii Y, Miller J. A, Burke M. P, Klippenstein S. J. J. Chem. Phys. A 2013;117(46):12146-12154

\*Corresponding author: luna.pratali@polimi.it

## π-HYDROGEN BONDING PROBES CHEMICAL REACTIVITY: BROMINATION OF CC DOUBLE BOND, ELECTROPHILIC AROMATIC NITRATION AND BENZYLATION

Boris Galabov,<sup>1</sup> Gergana Koleva,<sup>1</sup> Boriana Hadjieva,<sup>1</sup> Henry F. Schaefer III<sup>2</sup> <sup>1</sup>Department of Chemistry and Pharmacy, University of Sofia, Sofia 1164, BULGARIA; <sup>2</sup>Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602, UNITED STATES

Keywords

 $\pi$ -Hydrogen bonding, chemical reactivity, atomic charges, electrostatic potential, IR spectra

The reactivity trends for two basic organic reactions – addition of bromine to a CC double bond in alkenes and electrophilic aromatic nitration and benzylation– are rationalized using both experimental and theoretical quantities. Literature kinetic data are employed. The shifts of phenol O-H stretching frequency upon  $\pi$ -hydrogen bonding ( $\Delta v(OH)_{exp}$ ) with the nucleophilic reactants is shown to provide a quantitative measure of the reactivity for the considered reactions. Very good correlations between  $\Delta v(OH)_{exp}$  and theoretically estimated charge density parameters (atomic charges and shifts of molecular electrostatic potential) show that the O-H frequency shifts reflect the variations of nucleophilic properties in the reaction centers upon structural changes. The  $\Delta v(OH)_{exp}$  shifts perform much better in quantifying reactivity trends than usually employed experimental quantities, such as gas phase basicities and proton affinities.

#### References

1. Galabov B, Koleva G, Hadjieva B, Schaefer HF,  $\pi$ -Hydrogen Bonding Probes the Reactivity of Aromatic Compounds: Nitration of Substituted Benzenes, J Phys Chem A 2019;123; 1069–1076.

## Ignition Phenomena in Diethyl Ether/Air Mixtures: Elementary Steps, Mechanism, and Transport

Julia Eble, Johannes Kiecherer, Cornelie Bänsch, and Matthias Olzmann<sup>\*</sup> Institut für Physikalische Chemie, Karlsruher Institut für Technologie (KIT), Kaiserstr. 12, 76131 Karlsruhe, Germany

Keywords

Diethyl Ether, Autoignition, Ignition Delay, Cool Flames,

Diethyl ether (DEE) can be used as a diesel additive or an ignition improver. Furthermore, it is widely applied as a solvent, and hence its ignition behavior is of interest also under safety-engineering aspects. Depending on temperature and pressure, DEE/air mixtures show a great variety of ignition phenomena such as one- and two-stage ignition or cool flames.

In our contribution, we report on the determination of a number of rate coefficients of DEE reactions by laser-photolysis and shock-tube experiments and present a DEE oxidation mechanism that is valid over a broad range of temperatures (Eble et. al. 2017). The mechanism was tested by modeling experimental data from the literature with special attention on the temperature dependence of ignition delay times and two-stage ignition.

With this mechanism, autoignition of DEE in a spherical vessel with isothermal walls was simulated for different initial temperatures and pressures (program code INSFLA, see e. g. Maas and Warnatz 1988). Time-dependent profiles of temperature and species concentration were calculated with the system being treated as a one-dimensional laminar problem. Besides the homogeneous gas-phase reactions, surface reactions as well as transport of mass, energy, and momentum have been taken into account.

In this way, a mechanistic rationalization of different ignition phenomena like one-stage ignition, multiple-stage ignition and cool flames was possible. We give examples for these different phenomena, discuss the conditions of their occurrence, and map the corresponding p,T-ignition diagrams. We also discuss problems in identifying, classifying, and unambiguously naming the different ignition phenomena and point towards open problems relevant for low-T oxidation in general.

#### References

Eble J, Kiecherer J, Olzmann M. Low-Temperature Autoignition of Diethyl Ether/O<sub>2</sub> Mixtures: Mechanistic Considerations and Kinetic Modeling. Z Phys Chem 2017;231:1603–1623.

Maas U, Warnatz J. Ignition Processes in Hydrogen-Oxygen Mixtures. Combust. Flame 1988;74:53–69.

## BIOMASS-BURNING RELATED ATMOSPHERIC AQUEOUS-PHASE CHEMISTRY: KINETICS, PHOTOCHEMISTRY AND MODELLING

H. Herrmann, T. Schaefer, L. He, T. Felber, A. Tilgner and E.H. Hoffmann Atmospheric Chemistry Department (ACD), Leibniz Institute for Tropospheric Research (TROPOS), Permoserstrasse 15, 04318 Leipzig, GERMANY

#### Keywords

Aqueous phase, radicals, oxidation, triplet chemistry, kinetics, products, CAPRAM modelling, DFT.

Biomass burning (BB) is a phenomenon studied world-wide with increasing intensity. Recent results suggest that certain SOA products identified in particles originating from BB, have undergone aqueous-phase processing in aerosol-water containing particles, in haze or in clouds. Accordingly, we have studied numerous aqueous-phase reactions of relevance for these sub-systems in recent years in our laboratory and this contribution is giving an account of these studies.

Methoxyphenols are emitted from BB and may directly be oxidized through aqueous-phase reactions. Accordingly, temperature-dependent OH radical reactions have been investigated. Through the competition kinetics method using SCN<sup>-</sup>, rate constants for the reactions of OH have been determined for six substituted methoxyphenol. The reactions with OH are fast with,  $k_{298k} = (1.0 \pm 0.1) \times 10^{10}$  L mol<sup>-1</sup> s<sup>-1</sup> for 2-methoxyphenol. Kinetics of OH radical oxidation reactions of the BB related substituted benzoic acids have been studied and rate constants for 4 pairs of acids and their respective anions have been determined. For benzoic acid  $k_{298 \text{ K}, \text{ pH} = 1.5} = (3.7 \pm 0.1) \cdot 10^9$  L mol<sup>-1</sup> s<sup>-1</sup> and  $k_{298 \text{ K}, \text{ pH} = 8} = (4.0 \pm 0.2) \cdot 10^9$  L mol<sup>-1</sup> s<sup>-1</sup> were measured. These rate constants are moderately fast. For all OH kinetics, studied activation parameters are derived and rate constant compared to the diffusion limits calculated conventionally and by DFT.

To understand the impact of photosensitized reactions on BB SOA formation, different photosensitizers such as imidazole-2-carboxaldehyde (2-IC) and 3,4-dimethoxybenzaldehyde (DMB) were investigated regarding their photochemical properties. Therefore, trapping reactions were performed to determine the quantum yields of the excited triplet state of the photosensitizers  $(\phi(2-IC) = 0.85, \phi(DMB) = 0.37 \text{ at } \text{pH} = 5 \text{ and } \text{T} = 298 \text{ K})$  as well as spectroscopic studies to observe the excited triplet state formation at a specific time after the laser pulse ( $t_{delay} = 200 \text{ ns} - 500 \text{ } \mu$ s) resulting in time-resolved absorbance spectra ( $\lambda = 200 - 800 \text{ } \text{ nm}$ ).

All of the findings are expected to enhance the predictive capabilities of models such as the chemical aqueous-phase radical mechanism (CAPRAM). To understand the complex multiphase fate of oxygenated aromatic compounds, recently an aqueous-phase oxidation mechanism was developed. First multiphase chemistry model investigations of aromatic BB compounds revealed that the aqueous phase is an important media for oxidations as well as formation of higher nitrated aromatic compounds. Based on the existing aromatic module, it is planned to develop a dedicated BB aqueous-phase chemistry module.

## Effect of Methyl Group Substitution on the Kinetics of Vinyl Radical Oxidation

<u>Satya P. Joshi</u>, Timo T. Pekkanen, Raimo S. Timonen, Arkke J. Eskola<sup>\*</sup>

Department of Chemistry, University of Helsinki, P.O. Box 55(A.I. Virtasen aukio 1), FI-00014, Helsinki, Finland

Keywords

Radical reaction kinetics, Photo-ionization, mass-spectrometer, Unsaturated hydrocarbon fuel

#### Abstract

In order to understand the extensity of the effect of methyl group substitution on the kinetics of vinyl radical oxidation, the bimolecular rate coefficients of reactions  $(CH_3)_2CCH + O_2$  (1) and  $(CH_3)_2CCCH_3 + O_2$  (2) have been measured using a tubular laminar flow reactor coupled with a photoionization mass-spectrometer (PIMS). This study extends our investigations into the kinetics of methyl-vinyl radical oxidation.<sup>1</sup> These reactions are important for efficient and accurate modeling of unsaturated hydrocarbon fuels combustion. Pulsed excimer laser photolysis of brominated precursor molecule at 248 nm wavelength was used to produce radicals of interest. These experiments were performed at low pressure (0.4 - 2 Torr) over the temperature range of 223 - 600 K. The measured bimolecular rate coefficients for reactions (1) and (2) were found to be independent of bath gas pressure (concentration). For reaction (1), the bimolecular rate coefficients possess negative temperature dependence at low temperatures (T < 384 K) and appear to be independent of temperature at high temperatures (T > 384 K). The rate coefficients associated with reaction (2) exhibit the typical negative temperature dependency over the whole temperature range employed. Observed products of the reaction (1) were CH<sub>3</sub>COCH<sub>3</sub> and HCO while for the reaction (2) observed products were CH<sub>3</sub> and CH<sub>3</sub>COCH<sub>3</sub>. Methyl substitution of the vinyl radical changes its reactivity towards  $O_2$  downwards by ca. 50 % if the methyl groups takes both of the  $\beta$ -positions. The rate coefficients for reaction (2) were similar to that of vinyl radical.<sup>2</sup> This suggests that methyl group substitution to all  $\alpha$  and  $\beta$  position available to vinyl radical neutralizes the net effect of its reactivity towards O<sub>2</sub>. Performing a linear Arrhenius fit for the negative temperature dependency of observed bimolecular rate coefficients, the following rate expressions were obtained:  $k_1 = (1.52 \pm 0.4) \times 10^{-12} \exp(2.47 \pm 0.55 \text{ kJ mol}^{-1} / RT) \text{ cm}^3 \text{ s}^{-1} (T = 223 - 384 \text{ K}), k_2 = (3.42 \pm 0.1) \times 10^{-12}$  $\exp(2.35 \pm 0.12 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ s}^{-1} (T = 266 - 601 \text{ K}).$ 

#### References

1. Joshi SP, Pekkanen TT, Timonen RS, Lendvay G, Eskola AJ. Kinetics of the Methyl–Vinyl Radical +  $O_2$  Reactions Associated with Propene Oxidation. The Journal of Physical Chemistry A **2019**, *123*, 999-1006.

2. Eskola AJ, Timonen RS. Kinetics of the reactions of vinyl radicals with molecular oxygen and chlorine at temperatures 200–362 K. Phys. Chem. Chem. Phys. **2003**, *5*, 2557-2561.

\* Corresponding author: arkke.eskola@helsinki.fi

## EFFECT OF SURFACE–BULK PARTITIONING ON THE HETEROGENEOUS KINETICS OF AQUEOUS DROPLETS

Fabien Goulay,<sup>\*</sup> Hanyu Fan, and Tadini Wenyika Massaya, Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506, USA

Keywords

Heterogeneous, OH radical, atmospheric chemistry.

Multiphase processes in aerosols are known to affect the chemical composition of the atmosphere, its refractive ability, the process of cloud formation, and ultimately the climate. Models trying to reproduce and predict the chemical composition of the atmosphere are still limited by large uncertainties about chemical reactions occurring in the gas phase and in condensed aerosols. In particular, there is an urgent need to increase our understanding of reactions occurring at or near the gas–liquid interface.

Saccharide aqueous solutions display a wide range of surface tensions (Pegram and Record, 2009) and are used here as archetypal systems to determine the effect of partitioning on the heterogeneous kinetics of oxygenated molecules. In these studies, the OH-initiated heterogeneous oxidation of mixed organic aqueous aerosols is investigated using an atmospheric-pressure flow tube coupled to off-line analysis of the particle composition. For equimolar monosaccharide/disaccharide aqueous aerosol mixtures, the decay of the disaccharide is found to be significantly slower than that of the monosaccharide (Fan et al., 2019). Molecular dynamics simulations of the mixed aqueous solutions reveal the formation of a ~10 Å disaccharide exclusion layer below the water surface. A stochastic chemical model is developed to understand the possible effect of surface partitioning on the heterogeneous kinetics. The observed decays are consistent with a poor spatial overlap of the OH radical at the interface with the disaccharide in the particle bulk. The effect of partitioning on the heterogeneous oxidation of atmospheric organic aerosols is discussed.

#### References

Fan H, Masaya TM, Goulay F. Effect of surface–bulk partitioning on the heterogeneous oxidation of aqueous saccharide aerosols. Phys Chem Chem Phys 2019;21:2992–3001.

Pegram LM and Record MT. Using surface tension data to predict differences in surface and bulk concentrations of nonelectrolytes in water. J Phys Chem C 2009 ;113 :2171–2174.

## Kinetics of the Competing C–O Bond-Fission Reactions of Dimethoxymethane

Leonie Golka, Dennis Gratzfeld, Isabelle Weber, and Matthias Olzmann<sup>\*</sup> Institut für Physikalische Chemie, Karlsruher Institut für Technologie (KIT), Kaiserstr. 12, 76131 Karlsruhe, Germany

Keywords

Dimethoxymethane, Shock Tube, H-ARAS, Quantum Chemistry, Statistical Rate Theory

The reduction of soot and NO<sub>x</sub> emissions is one of today's major challenges for the automotive sector. In this context, oxymethylenethers (OME) are often discussed as potential diesel fuel substitutes/additives. For an adequate modeling of combustion and ignition processes of these OME/fuel mixtures, reliable kinetic data, especially for the initial reaction steps, is needed. As the smallest OME, dimethoxymethane (DMM) is particularly suited to study the reactivity of the characteristic methylenedioxy group (O–CH<sub>2</sub>–O). Under pyrolytic conditions, the decomposition of DMM predominantly proceeds via C–O bond-fission reactions yielding either CH<sub>3</sub>OCH<sub>2</sub>O + CH<sub>3</sub> or CH<sub>3</sub>OCH<sub>2</sub> + CH<sub>3</sub>O. Information on the branching ratio between these two reaction paths in the literature is scarce and contradictory.

In our contribution, we present the results of a combined experimental and theoretical study of the initial C–O bond-fission reactions of DMM. We studied the thermal decomposition of DMM behind reflected shock waves at temperatures between 1100 and 1600 K at three different nominal pressures between 0.3 and 4.7 bar, using H-atom resonance absorption spectroscopy (H-ARAS) for detection. Overall rate coefficients for the initial C–O bond-fission reactions were inferred from recorded H atom concentration-time profiles. A pronounced temperature and pressure dependence was observed.

For a detailed analysis of our experimental results, we characterized stationary points on the relevant potential energy surfaces with quantum-chemical calculations at the CCSD(F12\*)(T\*)/cc-pVQZ-F12//B2PLYP-D3/def2-TZVPP level of theory. To model the observed temperature and pressure dependence, we performed master-equation calculations with specific rate coefficients from the simplified Statistical Adiabatic Channel Model. On the basis of these results, an empirical parameterization of the temperature and pressure dependence is derived. The relative branching fractions for the initial reaction steps are deduced, and implications for combustion modelling are discussed.

### Atmospheric chemistry of iodous and iodic acids

S. Taamalli<sup>1,4,\*</sup>, D. Khiri<sup>1,4</sup>, S. Khanniche<sup>1,4</sup>, S. Suliman<sup>2</sup>, M. Ribaucour<sup>1,4</sup>, I. Cernusak<sup>2</sup>, L. Cantrel<sup>3,4</sup>andF. Louis<sup>1,4</sup>
<sup>1</sup>Univ. Lille, CNRS, UMR 8522-PC2A, PhysicoChimie des Processus de Combustion et de l'Atmosphère, 59000 Lille, France
<sup>2</sup>Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Ilkovičova 6,84215 Bratislava, Slovakia
<sup>3</sup>Institut de Radioprotection et de Sûreté Nucléaire (IRSN), PSN-RES, Cadarache, Saint-Paul Lez Durance 13115, France
<sup>4</sup>Laboratoire de Recherche Commun IRSN-CNRS-Lille "Cinétique Chimique, Combustion, Réactivité" (C3R), Cadarache, Saint-Paul Lez Durance, 13115, France

#### Keywords

Iodine chemistry, kinetic parameters, microhydration, atmospheric chemistry. nuclear safety.

In the case of an hypothetical nuclear accident, fission products are released into the environment. Simulation tools are commonly used to predict the radiological consequences on populations. After the Fukushima accident, significant differences have been observed between measured and modeled concentrations for iodine 131. This can be attributed to the high reactivity of iodine in the atmosphere not considered in the current dispersion crisis tools.

The purpose of this work is to provide a better understanding of the iodine chemistry using modeling tools such as theoretical chemistry calculations to supplement thermokinetic databases. Thermochemical properties ( $\Delta_f H^{\circ}(298 \text{ K})$ ,  $S^{\circ}(298 \text{ K})$ ,  $C_p(T)$ ) and kinetic parameters are needed as input parameters in the modeling. Such data are relatively scarce for iodine-containing species and some of them exhibit large uncertainties. Recently, Sipilä et al. reported evidence of iodine oxide particle formation.For instance, iodous acid has been measured in a field campaign at Mace Head in 2013 using a CI-APi-TOF (chemical ionization atmospheric pressure interface time of flight) mass spectrometer.Iodous acid concentration was about  $2 \times 10^6$  molecules cm<sup>-3</sup>.High concentrations of HIO<sub>3</sub> were observed with a vapour peak concentration greater than  $10^8$  molecules cm<sup>-3</sup> (Sipilä et al., 2016).

In this talkwe will present a brief review of our ongoing researches concerning the iodine oxides (HOIO, and HOIO<sub>2</sub>). For the first time, the microhydration processes have been studied to elucidate the role of hydrating water molecules. Rate constants were calculated using appropriate kinetic theories and their implications for both atmospheric chemistry and nuclear safety will be discussed.

#### References

M. Sipilä, N. Sarnela, T. Jokinen, H. Henschel, H. Junninen, J. Kontkanen, S.Richters, J. Kangasluoma, A. Franchin, O. Peräkylä, M.P. Rissanen, M. Ehn, H.Vehkamäki, T. Kurten, T. Berndt, T. Petäjä, D. Worsnop, D. Ceburnis, V.-M.Kerminen, M. Kulmala, C.D. O'Dowd, Molecular-scale evidence of aerosolparticle formation via sequential addition of HIO<sub>3</sub>, Nature (2016) 1–3, http://dx.doi.org/10.1038/nature19314.

## High-temperature shock tube ignition study of prenol isomers – "Hyperboosting" fuels relevant to the Co-Optima program

Erik Ninnemann, Andrew Laich, Sneha Neupane, Kyle Thurmond, and Subith Vasu

Center for Advanced Turbomachinery and Energy Research (CATER), Mechanical and Aerospace Engineering Department,

University of Central Florida, 4000 Central Florida Blvd, Orlando, FL 32816, USA

Keywords

Shock	Tube,	Ignition,	Prenol,	CO	time-history,	chemical	kinetics
-------	-------	-----------	---------	----	---------------	----------	----------

Alcohols are an attractive fuel alternative to current fossil fuels available on the market because they are readily available through renewable means and could decrease NOx emissions [1]. Prenol is an unsaturated alcohol that displays promise as a next generation biofuel or additive and hence is a considered candidate fuel under the Department of Energy's Co-Optimization of Fuels and Engines (Co-Optima) program. However, before these new fuels can be used in engines, their fundamental combustion properties must be studied. Prenol has a RON of ~94, however, when blended with gasoline prenol boosts RON above that of the base fuel, i.e., a "hyperboosting" effect for which the mechanism must be identified [2]. Therefore, towards this goal, CO time-histories are obtained during the oxidation of prenol and its isomer, isoprenol, behind reflected shockwaves in a shock tube at temperatures between 1269-1472 K and near 9.5 atm. Carbon monoxide timehistories for both fuels are compared to the simulations of the detailed kinetic mechanism of De Bruycker [3]. Current model predictions overpredicted both the ignition delay time and the max CO yield; however, the model captured the profile of CO formation well. Detailed uncertainty and sensitivity analyses were carried out to identify important reactions that need attention for accurate prediction of these fuel's chemistry. Further investigation into the rate of  $C_3H_3 + O_2=CH_2CO +$ HCO reaction was suggested based on current experiments. The experimental data and analysis presented here is critical in the development, validation and improvement of kinetic models of these promising Co-Optima fuels.

#### References

Al-Hasan M. Effect of ethanol–unleaded gasoline blends on engine performance and exhaust emission. energy conversion and management. 2003;44:1547-61.

Monroe E, Gladden J, Albrecht KO, Bays JT, McCormick R, Davis RW, et al. Discovery of novel octane hyperboosting phenomenon in prenol biofuel/gasoline blends. Fuel. 2019;239:1143-8.

De Bruycker R, Herbinet O, Carstensen H-H, Battin-Leclerc F, Van Geem KM. Understanding the reactivity of unsaturated alcohols: Experimental and kinetic modeling study of the pyrolysis and oxidation of 3-methyl-2-butenol and 3-methyl-3-butenol. Combustion and Flame. 2016;171:237-51.

## SHIELDING OF AEROSOL-BORNE PESTICIDES AGAINST OH RADICALS

Lei Han<sup>1</sup> and Cornelius Zetzsch<sup>1,2\*</sup>

<sup>1</sup>Multiphase Chemistry Department, Max Planck Institute for Chemistry, Hahn-Meitner-Weg 1, 55128 Mainz, GERMANY <sup>2</sup>Atmospheric Chemistry Research Unit, BayCEER, University of Bayreuth, 95448 Bayreuth,

GERMANY

Keywords

Heterogeneous reaction, persistent organic pollutants, atmospheric degradation, OH radicals.

The heterogeneous reaction of OH with semivolatile organic compounds has been investigated on various surfaces. A chemically inert surface and a low coverage by the test compound are desirable in order to avoid a loss of OH by reaction with the adsorbent and a passivation by reaction products (which can be less reactive and may reside on the uppermost layer). Mattei et al. (2019) exposed eight pesticides (deltamethrin, permethrin, pendimethalin, cyprodinil, oxadiazon, fipronil, tetraconazole and difenoconazole) on Aerosil particles to OH radicals in a rotating bulb reactor and observed a slow consumption of deltamethrin, permethrin and pendimethalin on hydrophilic fused silica (Aerosil 225) and a significantly slower one on the hydrophobic Aerosil R812. On the other hand, no consumption of the other five pesticides by OH occurred at all, leading to the conclusion that the pesticides are POPs (persistent organic pollutants) in contrast to the expectation from well-known structure/reactivity relations.

In this study, we exposed the herbicide terbuthylazine (TBA) as aerosol coating on three different types of silica particles (the hydrophilic Aerosil 200, the hydrophobic Aerosil R812 and Stöber-SiO<sub>2</sub>) to OH radicals (after atomizing aqueous suspensions of the coated particles into an aerosol chamber). More than 80% of the OH was found to be scavenged in reactive aggregates of Aerosil R812 (as compared to Aerosil 200 in accord with the shielding effects by OH-reactive surfaces described by Socorro et al., 2017). This may explain the lower reactivity on hydrophobic Aerosil R812, due to the lack of degradation and apparent persistence in the less porous bulk of Aerosil R812. Although our aerosol chamber experiments with coated Stöber-SiO<sub>2</sub> (up to a monolayer of TBA) quantified a minor self-shielding effect against OH by bulky TBA in less porous aggregates (our primary particles have a diameter of around 160 nm), we cannot confirm TBA to be persistent based on the 2-days atmospheric half-life limit of the Stockholm convention.

#### References

Mattei, C, Wortham, H, Quivet, E. Heterogeneous Degradation of pesticides by OH radicals in the atmosphere: Influence of humidity and particle type on the kinetics. Sci. Total Environ. 2019; 664: 1084-1094.

Socorro, J, Lakey, PS, Han, L, Berkemeier, T, Lammel, G, Zetzsch, C, Pöschl, U, Shiraiwa, M. Heterogeneous OH oxidation, shielding effects, and implications for the atmospheric fate of terbuthylazine and other pesticides. Environ. Sci. Technol. 2017; 51: 13749-13754.

\*Corresponding author: cornelius.zetzsch@mpic.de

## Ignition delay times of dibutylether in a Rapid Compression Machine

Fethi Khaled<sup>1</sup>\*, Zeynep Serinyel<sup>2,3</sup>, Guillaume Dayma<sup>2,3</sup>, Fabrice Foucher<sup>1,3</sup> <sup>1</sup>Laboratoire Pluridisciplinaire de Recherche en Ingénierie des Systèmes, Mécanique, Energétique (PRISME), Université d'Orléans, 8 Rue Leonard de Vinci, 45072 Orléans Cedex, France

<sup>2</sup>Institut de Combustion Aérothermique Réactivité et Environnement (ICARE), Centre National de la Recherche Scientifique (CNRS)-Institut des Sciences de l'Ingénierie et des Systèmes (INSIS), 1C Avenue de la Recherche Scientifique, 45071 Orléans Cedex 2, France

<sup>3</sup>Université d'Orléans, Château de la Source, 45100 Orléans, France

#### Keywords

Ignition delay time, rapid compression machine, dibutylether, chemical kinetics, biofuels

Ignition delay times (IDTs) of fuels provide very important macro-information about their reactivity and auto-ignition behavior. In the last decade, Interests in bio-fuels have increased due to their relative availability and also their low carbon fingerprint. Dibutylether (DBE) is a second generation biofuel that can be produced through biomass pulping processes and which is proven to help reduce more than 70% CO<sub>2</sub> emission compared to commercial diesel fuels (Damyanov et al. 2018). In this work, we provide ignition delay time measurements of DBE in a rapid compression machine (RCM) at conditions that spanned the temperature range 550 -800 K, the pressure range 3 - 10 bar and the equivalence ratio range 0.5 - 2. The particular kinetic properties of DBE that makes it highly reactive are discussed. Data of the 1<sup>st</sup> stage ignition delay time of DBE measured in the RCM are used to update a published kinetic model of DBE that was previously developed based on jet-stirred reactor and laminar flame speeds (Thion et al. 2017 and Cai et al. 2014). In the RCM, complexity of the heat losses downstream the 1<sup>st</sup> stage ignition delay time limits the possibility of using the adiabatic core assumption for comparison with zero-dimensional (0-D) simulations. These challenges are illustrated through experimental ignition profiles and their implications on the total IDT of DBE are discussed. 0-D simulations were performed to identify the sensitive kinetic routes that affect the cool flame formation of DBE at the conditions of the RCM. The identified pathways are then refined accordingly.

#### References

Thion, S.; Togbé, C.; Serinyel, Z.; Dayma, G.; Dagaut, P., A chemical kinetic study of the oxidation of dibutyl-ether in a jet-stirred reactor. Combust. Flame 2017, 185, 4-15.

Cai, L.; Sudholt, A.; Lee, D. J.; Egolfopoulos, F. N.; Pitsch, H.; Westbrook, C. K.; Sarathy, S. M., Chemical kinetic study of a novel lignocellulosic biofuel: Di-n-butyl ether oxidation in a laminar flow reactor and flames. Combust. Flame 2014, 161 (3), 798-809.

Damyanov, A.; Hofmann, P.; Geringer, B.; Schwaiger, N.; Pichler, T.; Siebenhofer, M., Biogenous ethers: production and operation in a diesel engine. Automotive and Engine Technology 2018, 3 (1), 69-82.

#### Polymer mixtures thermal degradation kinetic analysis

Briceno J, Lemos M.A.N.D.A, Lemos F.\*

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

Lisoou, i oltugui

Keywords: Thermal degradation, kinetic analysis, model-fitting method, thermogravimetric analysis, PP, HDPE.

Chemical recycling has been a method of extent studies due to the plastics environmental issue worldwide. Pyrolysis has been identified as an interesting method to handle plastic wastes through chemical recycling. The thermal degradation kinetics was studied for 2 different types of plastics, High Density Polyethylene (HDPE) and Polypropylene (PP), both separately and mixed in different proportions. Thermal degradation was performed using thermogravimetric analysis (TGA) with simultaneous differential scanning calorimetry (DSC) in a non-isothermal process under an inert atmosphere. A model-fitting approach was used to obtain the kinetic parameters for the thermal degradation.

The results show that the HDPE has a higher degradation temperature than the PP. The results show that the mixture starts to degrade at lower temperatures than pure components (see figure 1a). The estimated apparent activation energy was higher with the pure polymers, (higher for pure HDPE), and reached a minimum at around 35% HDPE content (as seen in figure 1b). Similar results were also obtained for LDPE-PP mixtures.



Figure 1. a) TGA profile for pure HDPE, PP and 65% HDPE-35% PP mixture. b) Estimated apparent activation energy for the mixture (obtained by model fitting) vs percentage of HDPE in a PP-HDPE blend.

#### Acknowledgments

The authors thank FCT for financial support through CERENA (project UID/ECI/04028/2019) and project PTDC/EQU-EQU/29614/2017.

#### References

Murichan N, Cherntongchai P. Kinetic Analysis of Thermal Degradation of Polyolefin Mixtures. Int J Chem Eng Appl 2015; 5: 169-175.

Vyazovkin S, Wight CA. Model-free and model- fitting approaches to kinetic analysis of isothermal and nonisothermal data. Thermochim Acta. 1999; 340-341: 53–68.

\* Corresponding author: francisco.lemos@tecnico.ulisboa.pt

## CO FORMATION FROM DIMETHYL-CARBONATE PYROLYSIS BEHIND REFLECTED SHOCK WAVES

Olivier Mathieu<sup>\*</sup>, Clayton R. Mulvihill and Eric L. Petersen J. Mike Walker '66 Department of Mechanical Engineering, Texas A&M University College Station, TX 77843 USA

Keywords: Shock tube, CO laser absorption, pyrolysis, Dimethyl-Carbonate

Dimethyl-carbonate, or DMC,  $(H_3CO-CO-OCH_3)$  is a non-toxic carbonate ester produced from biomass. When used as an additive to diesel fuel, DMC leads to reductions in both  $CO_2$  and soot particle emissions. Over the past 15 years, several detailed kinetics models for DMC have

been published (Glaude et al., 2005, Hu et al., 2015, Sun et al., 2016, Alexandrino et al., 2018). To improve the combustion chemistry of DMC, the CO formation from the pyrolysis of a dilute mixture of DMC was investigated between 1230 and 1560 K, at around 1.5 atm, in a shock tube using laser absorption at 2190.0175 cm<sup>-1</sup>. To the best of the authors' knowledge, the data presented herein are the first laser-absorption measurements for DMC pyrolysis products.

As can be seen in Fig. 1, while only the two most recent models provide relatively good predictions, more work is still necessary to further develop the combustion chemistry of DMC. A numerical





analysis (sensitivity, rate of production, and reaction pathway analyses) was performed with the model from Alexandrino and coworkers. Key reactions were identified, and suggestions are provided to improve the accuracy of the model.

#### References

Alexandrino K, Alzueta MU, Curran HJ. An experimental and modeling study of the ignition of dimethyl carbonate in shock tubes and rapid compression machine. Combust. Flame 2018;188:212-226.

Glaude PA, Pitz WJ, Thomson MJ. Chemical kinetic modeling of dimethyl carbonate in an opposed-flow diffusion flame. Proc. Combust. Inst. 2005;30:1111-1118.

Hu E, Chen Y, Zhang Z, Pan L, Li Q, Cheng Y, Huang Z. Experimental and kinetic study on ignition delay times of dimethyl carbonate at high temperature. Fuel 2015;140:626-632.

Sun W, Yang B, Hansen N, Westbrook CK, Zhang F, Wang G, Moshammer K, Law CK. An experimental and kinetic modeling study on dimethyl carbonate (DMC) pyrolysis and combustion. Combust. Flame 2016;164:224-238.

\*Corresponding author: olivier.mathieu@tamu.edu

## THEORETICAL AND EXPERIMENTAL STUDIES OF THE THERMAL OXIDATION OF EPOXY-AMINE SYSTEMS

Romain Delannoy<sup>1,2,\*</sup>, Emmanuel Richaud<sup>1</sup> and Vincent Tognetti<sup>2</sup> <sup>1</sup>Laboratoire PIMM, Arts et Métiers, CNRS, Cnam, Hesam Université, 151 boulevard de l'hôpital, 75013 Paris, FRANCE <sup>2</sup>Normandy University, COBRA UMR 6014, Université de Rouen, INSA Rouen, CNRS, 1 rue Lucien Tesnière, 76821 Mont St Aignan Cedex, FRANCE

Keywords

Thermal oxidation, epoxy resin, FTIR, DFT calculations

Commonly used as a matrix for coatings and fiber-reinforced composite materials, the thermal oxidation of epoxy resins has been studied over the past decades to predict their lifetime. Molecular and macromolecular changes have been previously investigated to understand the origin of mechanical failure (Ernault et al., 2017).

The current presentation aims to better understand the mechanisms occurring during the oxidation process, to implement a kinetic model, and to identify reactive intermediates responsible for the material degradation. As such, a series of experimental analyses and quantum chemistry calculations using density functional theory (DFT) have been carried out.

Epoxy systems investigated in this study were obtained by curing DGEBA with three similar amine hardener components ethylenediamine EDA, diethylenetriamine DETA, and triethylenetetramine TETA. Oligomer epoxy systems based out of epoxy phenoxypropane EPP were also used to simplify DFT calculations as a first approach, and to discuss on the effect of mobility on oxidation kinetics.

Oxidation of epoxy samples was shown to generate carbonyl and amide groups monitored by FTIR spectroscopy. Results were discussed using DFT, allowing BDE calculations of C-H bonds on oxidizable sites. Those were used to assess the most likely elementary mechanisms occurring during the thermal degradation.

The authors gratefully acknowledge financial support and funding from the National Research Agency (ANR) for this study through the project "DUREVE" (2019-2022).

#### References

Ernault E, Richaud E, Fayolle B. Origin of epoxies embrittlement during oxidative ageing. Polym Test 2017;63:448-454.

# Shock tube study of the pyrolysis kinetics of di- and trimethoxy methane

Malte Döntgen<sup>1</sup>, Mark E. Fuller<sup>1</sup> and C. Franklin Goldsmith \*1

<sup>1</sup>School of Engineering, Brown University, Providence, RI 02912, USA

#### Keywords

Diaphragmless shock tube, oxymethylene ethers, pyrolysis, high temperature, subatmospheric pressure

The growing demand for alternative fuels, such as biofuels, has recently opened up a new field of research: The production and combustion of oxymethylene ethers (OMEs). [1, 2] Scientists from all over the world see high potential in these compounds, despite difficulties in using them as drop-in fuels. The high oxygen-to-carbon ratio of these fuels make them burn clean and enable production routes from oxygenated reactants. Understanding the reaction kinetics of the smallest OME, dimethoxy methane (DMM), and its derivative trimethoxy methane (TMM) will aid understanding the overall combustion behavior of these alternative fuels.

We use the shock tube facility at Brown University to investigate the pyrolysis kinetics of DMM and TMM under high-temperature (> 1200 K) and sub-atmospheric pressure (30-120 Torr) conditions. The shock tube is diaphragmless and utilizes a fast acting valve to produce shock waves, rather than rupturing a diaphragm. A laser-schlieren densitometry optical diagnostic records density gradient profiles versus time, allowing for determination of the rate of heat release and subsequent determination of reaction kinetics. Therefore, this setup allows us to investigate the inception stage of DMM and TMM pyrolysis.

The experiments are supported by quantum chemical calculations of the fuel molecules and their dissociation reactions. This allows to directly compare calculated and measured elementary rate constants. Despite the structural differences between DMM and TMM at the central carbon (secondary *vs.* tertiary, respectively), the main pyrolysis pathways are very similar: DMM to methanol and methyl formate and TMM to dimethyl ether and methyl formate.

#### References

Kopp WA, Kröger LC, Döntgen M, Jacobs S, Burke U, Curran HJ, Heufer KA, Leonhard K. Detailed kinetic modeling of dimethoxymethane. Part I: *Ab initio* thermochemistry and kinetics predictions for key reactions. Combust Flame 2018;189:433-442

Jacobs S, Döntgen M, Alquaity ABS, Kopp WA, Kröger LC, Burke U, Pitsch H, Leonhard K, Curran HJ, Heufer KA. Detailed kinetic modeling of dimethoxymethane. Part II: Experimental and theoretical study of the kinetics and reaction mechanism. Combust Flame 2019;In Press:10.1016/j.combustflame.2018.12.026

<sup>\*</sup>Corresponding author: franklin\_goldsmith@brown.edu
#### Thermal and catalytic degradation of polypropylene with VGO and UCO

<u>Godinho T.<sup>1</sup></u>, Lemos M.A.N.D.A.<sup>1</sup>, Carabineiro H.<sup>2</sup>, Tarelho L.<sup>3</sup> and Lemos.F<sup>1,\*</sup> <sup>1</sup>CERENA, Instituto Superior Técnico, 1049-001 Lisboa, Portugal

CEREINA, Instituto Superior Tecinico, 1049-001 Lisboa, Portuga

<sup>2</sup>Galp Energia, Refinaria de Sines, Apartado 15, 7520-952 Sines, Portugal

<sup>3</sup>CESAM, Universidade de Aveiro, 3810-193 Aveiro, Portugal

#### Keywords: Kinetic analysis, Pyrolysis, Polypropylene, Vacuum gas oil, Unconverted oil, Co-processing

In recent years, problems such as global warming are worsening due to the increase in population, greater dependence on fossil fuels and the accumulation of waste (British Petroleum, 2018). This type of problems can be minimized through the partial substitution of fossil fuels and the effective use of available plastic waste. This work will focus on tertiary recycling of plastic waste, more specifically on the pyrolysis of polypropylene (PP), in coprocessing with vacuum gas oil (VGO), unconverted oil (UCO) with the objective of checking the feasibility of performing a co-processing between PP and the feed of a Fluid Catalytic Cracking (FCC) unit. The pyrolysis was carried-out in a simultaneous TG/DSC equipment. Experiments were performed at different heating rates, with different types of catalysts (Spent FCC, HZSM-5 and H-beta) and different catalyst/hydrocarbon mass ratios. Model free methods and isoconversional methods (Aboulkas, El, & Bouadili, 2010) were applied to the resulting DSC-TGA data in order to identify the most suitable reaction model and estimate the relevant kinetic parameters. The results of this work show that the temperature, corresponding to the maximum rate of degradation of each compound studied, increases with: the increase of the heating rate (when this is low) and the decrease of the catalyst mass. It is found that in the coprocessing of the PP with the other compounds, the relation between the degradation temperatures is not linear with the mass variation of the compounds. In addition, the kinetic parameters obtained are within the values established by the literature.



**Figure 1-** Normalized DTG curve for the thermal analysis, under inert atmosphere, of UCO, VGO, PP and mixtures (PP+VGO and PP+UCO) with a heating rate of 10 °*C*/min.

#### References

Aboulkas A, El harfi K, Bouadili AEl. Thermal degradation behaviors of polyethylene and polypropylene. Part I: Pyrolysis kinetics and mechanisms. Energy Conv Manag (2010). 51(7): 1363–1369.

British Petroleum. (2018). BP Statistical Review of World Energy.

#### Acknowledgements

The authors would like to thank FCT for financial support through CERENA (strategic project UID/ECI/04028/2019) and project PTDC/EQU-EQU/29614/2017.

\*Corresponding author: francisco.lemos@tecnico.ulisboa.pt

### OXIDATION OF AN ISO-PARAFFINIC ALCOHOL-TO-JET FUEL AND HEPTANE MIXTURE: AN EXPERIMENTAL AND MODELLING STUDY

Juan Guzman<sup>1</sup>, Goutham Kukkadapu<sup>2</sup>, Kenneth Brezinsky<sup>1,\*</sup> and Charles Westbrook<sup>2</sup> <sup>1</sup>Department of Mechanical and Industrial Engineering, University of Illinois at Chicago, Chicago, IL 60607, USA

<sup>2</sup>Lawrence Livermore National Laboratory, Livermore, CA 94551, USA

Keywords

Shock tube, ATJ, heptane, high pressure, oxidation.

The High Pressure Shock Tube Laboratory has two shock tubes which are used for the chemical kinetic analysis of the decomposition of hydrocarbon propulsion fuels, both oxidatively and pyrolytically. Between the two shock tubes, a wide range of pressures can be covered since, in combination, they can operate from sub atmospheric to 1000 bar. The lower pressure tube operates at pressures below 15 bar, and the high pressure tube operates from 15 to 1000 bar. Both shock tubes were used to analyze the oxidation of alcohol-to-jet (ATJ) fuel/*n*-heptane mixtures. Three sets of experiments were performed at two different pressures (4 and 50 bar), different fuel loadings (~100-1400 ppm), and slightly rich conditions ( $\phi$ =1.27-1.36). To compare how these two fuels interact with each other, two more sets of experiments were performed for pure ATJ and pure *n*-heptane matching the conditions of the high pressure ATJ/*n*-heptane mixture experiments. The intermediate species were quantified using gas chromatography coupled to a flame ionization detector and a thermal conductivity detector. The effects of pressure and fuel loading are discussed and presented in this study. Furthermore, the experimental measurements of each case are compared against the simulations of the detailed iso-alkane kinetic model from Lawrence Livermore National Laboratory. The modeling results are further discussed to show the effects of pressure and fuel loading.

\*Corresponding author: kenbrez@uic.edu

## **Fundamentals of Polymer Fouling in Ethylene Crackers**

Michael Forsuelo<sup>1</sup>, Duminda Ranasinghe<sup>1</sup>, Hao-Wei Pang<sup>1</sup>, Lawrence Lai<sup>1</sup>, Mica Smith<sup>1</sup>, Mark Goldman<sup>1</sup> and William H. Green <sup>\*1</sup>

<sup>1</sup>Department of Chemical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA

#### Keywords

Polymer Fouling, Automated Chemical Kinetics, Reaction Mechanism Generator (RMG), Complete Basis Set Methods (CBS-QB3), (Variational) Transition State Theory

Polymer fouling is a ubiquitous problem in ethylene cracking plants. Butadiene is an active conjugated diene that readily polymerizes at typical process conditions in the presence of active oxygen or free radical species. This monomer along with other compounds can form polymers that deposit in downstream equipment resulting in sub-optimal operation and eventual plant shut down. A variety of empirical approaches have been developed and used, with mixed success, to ameliorate process fouling. Nevertheless, there is limited fundamental understanding on the origin and mitigation of fouling.

In this work, we lay the foundations for understanding polymer fouling with Reaction Mechanism Generator (RMG), a software package that constructs detailed chemical reaction mechanisms automatically. We address the problem hierarchically, establishing the pure 1,3-butadiene kinetics and iteratively perturbing with chemistries suspected for fouling.

RMG automatically identifies the dimerization and isomerization pathways of pure 1,3-butadiene to 4-vinylcyclohexene, 1,5-cyclooctadiene, and 1,2-divinylcylobutane and minor polymerization pathways at debutanizer (DC<sub>4</sub>) reboiler conditions (Yan 2000). The fidelity of the model is refined with high-level quantum mechanical calculations. Closed- and open-shell species are evaluated with CBS-QB3 at stationary points. Transition states and connected local minima are verified with Intrinsic Reaction Coordinate (IRC) calculations. Barrier and barrierless reaction kinetics can be calculated with Transition State Theory (TST) and Variable Reaction Coordinate Variational Transition State Theory (VRC-VTST), utilizing software packages Arkane and Polyrate 17 (Bao & Truhlar 2017). Experimental designs to verify RMG models are proposed, including (semi-)batch operation of stainless steel pressure vessels with optical spectroscopy and GCxGC-MS techniques. Initial assessments are presented on a subset of perturbative chemistries, namely (in)active oxygen and olefin and paraffin co-elutants. In future work, the remaining perturbative chemistries and mitigation strategies will be investigated. This task entails the automation of condensed-phase and heterogeneous kinetics within RMG.

#### References

Yan M. Simulation and Optimization of an Ethylene Plant. Master's thesis, Texas Tech University, 2000, TTU Electronic Thesis and Dissertation collection.

Bao JL, Truhlar DG. Variational Transition State Theory. Chem Soc Rev 2017;46(24):7548-7596.

\*Corresponding author: whgreen@mit.edu

## **Reaction Kinetics of Hydroxyl Radicals with Dienes**

Aamir Farooq<sup>1</sup> and Binod Giri<sup>1</sup>

Clean Combustion Research Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia

Keywords

Dienes, Hydroxyl radicals, Rate coefficients, Shock tube, Laser absorption.

The combustion chemistry of hydrocarbons is a complicated phenomenon, the nature of which not only depends on the intrinsic chemical properties of hydrocarbons but also on the thermodynamic conditions of temperature and pressure. A common theme across combustion and atmospheric environments, however, is the highly active role played by hydroxyl radicals in the chain propagation and chain branching pathways. The reactions of OH radicals with hydrocarbons display quite an interesting kinetic beyhavior. For saturated hydrocarbons + OH system, only hydrogen abstraction reactions are feasible. The severity of the temperature dependence of such a system depends on the available chemical environments of the abstractable hydrogen atoms. In contrary, OH radical reactions with unsaturated hydrocarbons often exhibit complex kinetics as a result of many available chemical pathways, e.g., abstraction, addition and non-abstraction bimolecular pathways in such a convoluted chemical system. Recently, we have investigated the reactions of hydroxyl radicals with a range of diolefins to unravel the kinetics of such chemical systems over a wider range of conditions. Our work combined high-temperature experiments in a shock tube with low-temperature experiments in a flow reactor to gain new insights into the temperature dependance of these reactions. Particularly, this talk will elaborate on the observed reactivity differences between the reactions of conjugated and unconjugated diolefins with OH radicals. Interestingly, in contrast to other conjugated diolefins, 1,4pentadience exhibited a significant contribution from the H-abstraction channels even at low temperatures, and this behavior is explained by high-level *ab initio* and ME/RRKM methods.

#### References

- F. Khaled, B.R. Giri, D. Liu, E. Assaf, C. Fittschen, A. Farooq, "Insights into the reaction of hydroxyl radical with diolefins from atmospheric to combustion environments", Journal of Physical Chemistry A 123 2261 – 2271 (2019)
- F. Khaled, J. Badra, A. Farooq, "A shock tube study of C4 C6 straight chain alkenes + OH reactions", Proceedings of the Combustion Institute 36 289 298 (2017)
- 3. F. Khaled, B.R. Giri, D. Liu, A. Farooq, "On the reaction of OH radicals with C2 hydrocarbons", Proceedings of the Combustion Institute 37 213 219 (2019)

<sup>\*</sup>Corresponding author: aamir.farooq@kaust.edu.sa

## REVEALING THE ORIGIN OF THE CATALYTIC POWER OF ENZYMES BY MERGING COMPUTATIONAL STUDIES AND EXPERIMENTS

Sergio Martí, Raquel Castillo, Katarzyna Świderek, Maite Roca, Kemel Arafet, Daria De Raffele, Natalia Serrano, Miquel A. Galmes and Vicent Moliner.<sup>\*</sup> Departament de Química Física i Analítica, Universitat Jaume I, 12071 Castelló, SPAIN.

Keywords

QM/MM, MD, enzyme catalysis, enzyme design, enzyme inhibitors

Computational Chemistry techniques based on the combination of Quantum Chemistry and classical Molecular Mechanics (QM/MM) have been extensively applied to the study of enzyme catalysis. Merging these techniques with experimental methods has allowed to acquire a deep knowledge of the reaction mechanisms of these complex but highly efficient biocatalysts at the molecular level.

We will focus in this communication on aspects such as the controversial debate on whether protein dynamics are linked to the chemical reaction step,<sup>1</sup> the role of the quantum tunneling and the electrostatic effects contributions to catalysis,<sup>2</sup> or the relevance of compression effects in enzymatic methyl transfer reactions.<sup>3</sup>

The information acquired from studies of wild type enzymes can be exploited by industry since these gigant molecules are able to perform difficult synthetic reactions without the need of extreme temperatures, high pressures or toxic chemicals.<sup>4</sup> In addition, the detailed knowledge of enzymatic processes at molecular level can be the bedrock in the design of new drugs.<sup>5</sup>

Recent results obtained in our laboratory in these different lines of research, in collaboration with other groups, will be summarized in this communication.

#### References

1. Luk, L.Y.P. et al. Proc. Nat. Acad. Sci. USA. 2013, 110, 16344–16349.

2. Krzemińska, A.; Moliner, V.; Świderek, K. J. Am. Chem. Soc. 2016, 138, 16283–16298.

3. Świderek, K.; Tuñón, I.; Williams, I.H.; Moliner, V. J. Am. Chem. Soc. 2018, 140, 4327–4334.

4. (a) Świderek, K.; Tuñón, I.; Moliner, V.; Bertran, J. Arch. Biochem. Biophys. 2015, 582, 68–79. (b) Nödling, A.R. et al. Angew. Chem. Int. Ed. 2018, 57, 12478–12482.

5. (a) Kholodar, S. A.; Ghosha, A. K.; Świderek, K.; Moliner, V.; Kohen, A. Proc. Natl. Acad. Sci. USA. 2018, 115, 10311–10314. (b) Ren, R.; et al. Nature Commun. 2018, 9, Article number: 3243. (c) Serrano-Aparicio, N.; Świderek, K.; Moliner, V. Eur. J. Med. Chem. 2019, 164, 399–407.

## SHOCK-TUBE MEASUREMENTS OF CO CONCENTRATION TIME-HISTORIES DURING ISO-OCTANE OXIDATION

Olivier Mathieu<sup>\*</sup>, Sean Cooper, Sulaiman Alturaifi, Clayton R. Mulvihill and Eric L. Petersen J. Mike Walker '66 Department of Mechanical Engineering, Texas A&M University College Station, TX 77843 USA

Keywords

Shock tube, CO laser absorption, iso-octane.

Iso-octane ( $C_8H_{18}$ ) is a branched paraffin that is used, along with n-heptane, to measure the RON and MON values of gasoline fuels. It is also a component commonly used in gasoline fuel surrogates, to represent the iso-alkane fraction (Sarathy et al., 2018). It is therefore not

surprising that many studies have investigated the combustion chemistry of iso-octane, notably its ignition delay time and laminar flame speed (Atef et al., 2017), both being important combustion parameters for gasoline engines. While global kinetics data such as ignition delay time and laminar flame speed are necessary to tune the reactivity of detailed kinetics mechanisms, spectroscopic measurements of key species allow one to further constrain and improve these models. To that end, CO time histories were measured using laser absorption (Fig. 1) for the first time in a shock tube with iso-octane. Three equivalence ratios were investigated (0.5, 1.0, and 2.0) at a



Figure 1: Experimental CO profiles from iso-octane at various equivalence ratios.

pressure of around 1.5 atm (99% dilution). A numerical analysis was performed with models from the literature to identify the most important reactions for CO formation. Recommendations are made to improve the accuracy of the models based on this analysis.

#### References

Atef N, Kukkadapu G, Mohamed SY, Al Rashidi M, Banyon C, Mehl M, Heufer KA, Nasir EF, Alfazazi A, Das AK, Westbrook CK, Pitz WJ, Lue T, Farooq A, Sung C-J, Curran HJ, Sarathy MS. A comprehensive iso-octane combustion model with improved thermochemistry and chemical kinetics. Comb. Flame 2017:178:111–134.

Sarathy SM, Farooq A, Kalghatgi GT. Recent progress in gasoline surrogate fuels. Prog. Energy Comb. Science 2018:65:67-108.

\*Corresponding author: olivier.mathieu@tamu.edu

#### TG/DSC Analysis of the Pyrolysis Kinetics of Polystyrene from WEEE

Kol de Carvalho R., Rijo B., Rey F., Carvalho T., Lemos F., Lemos M.A.N.D.A.\* CERENA, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

#### Keywords: Kinetic study; Thermal Pyrolysis, Polystyrene, WEEE plastic

The waste of electrical and electronic equipment (WEEE) is currently considered to be one of the fastest growing waste streams in Europe, growing at 3-5 % per year [Eurostat (2017)]. In 2015, the quantity of WEEE amounted to 9.5 million tonnes per year, of which 1.2 million tonnes were plastic materials. Polystyrene (PS) is one of the plastics found in WEEE [EERA (2017)]. The challenge of recycling of WEEE lies on the complicated recycling process due to the existence of diverse plastic materials and additional additives [EERA (2017)]. Thermal pyrolysis is an attractive option for plastic waste management due to its particularity of converting plastic waste into valuable feedstock for the chemical industry and treat mixed and unwashed plastic wastes [Scheirs and Kaminsky (2006)]. The kinetics of thermal degradation of virgin PS and of waste PS from WEEE, before and after plastic separation pre-treatment, was investigated by thermogravimetric analysis coupled with differential scanning calorimetry (TG/DSC) and in a bench scale reactor. The influence of the heating rate and temperature on the thermal decomposition was studied. The decomposition of virgin PS showed one degradation peak and a single-first order model was applied (Fig. 1). The degradation of waste PS showed two decomposition peaks and therefore more complex models were tested. A twocomponent degradation model provides an adequate description of the experimental data (Fig. 2). Different kinetic schemes were tested. The best fitting models were applied for different heating rates in order to ensure that a single set of kinetic parameters described the ensemble of the data.



Figure 1 - DTG from virgin polystyrene.



#### Acknowledgments

The authors thank FCT for financial support through CERENA (project UID/ECI/04028/2019) and project PTDC/EQU-EQU/29614/2017. Also, to Ambigroup for the WEEE samples.

#### References

Eurostat: https://ec.europa.eu/eurostat/web/waste/key-waste-streams/weee. Accessed 20/2/2019.

European Electronics Recyclers Association (EERA), Report on EERA' s comments and proposals for the EU Plastics Strategy 2017, 2017.

\*Lemos, M.A.N.D.A.: mandal@tecnico.ulisboa.pt

## Dual-comb spectroscopy in shock tubes: Mid-Infrared microsecondresolved spectrometer

A. Hugi<sup>1,\*</sup>, M. Geiser<sup>1</sup>, R. Horvath<sup>1</sup>, C. L. Strand<sup>2</sup>, N. Pinkowski<sup>2</sup>, Y. Ding<sup>2</sup> and R. K. Hanson<sup>2</sup> <sup>1</sup> IRsweep AG, Laubisrütistr. 44, 8712 Stäfa, Switzerland

<sup>2</sup> High Temperature Gasdynamics Laboratory, Department of Mechanical Engineering, Stanford University, 452 Escondido Mall, Stanford, California 94305, United States

Keywords Time-resolved spectroscopy, single-shot spectroscopy, mid-infrared, combustion diagnostic

Infrared laser spectroscopy has been a successful tool in studying time-resolved processes in combustion (Hanson et al., 2016) and a variety of other fields. Traditional laser systems emit a single wavelength at a given time and wavelength tuning rates and ranges are limited.

In contrast, the method of dual-comb spectroscopy employs broadband mode locked lasers emitting many wavelengths simultaneously enabling studies of the time evolution of multiple molecular absorption features simultaneously. The recent advent of Quantum Cascade Laser (QCL) based mid-IR frequency combs (Hugi et al., 2012) and the demonstration of their suitability for dual-comb spectroscopy (Villares et al., 2014) led to the integration of the technique into a spectrometer.

Adaption of the method to a shock tube is reported. It was used to paint a detailed picture of a 1.0 ms high-temperature reaction between propyne and oxygen. The accuracy of the spectrometer was confirmed using a suite of independent laser diagnostics and indicates an auspicious future for DCS in high-energy reaction kinetics.



Figure 1 Left: Illustration of a shock tube equipped with a QCL dual-comb spectrometer. Middle: Dual-comb-measuredabsorbance spectrum of Single-shot measurements of propyne oxidation. Right: Speciation measurements and simulated results for propyne and water

#### References

Hanson, R. K., Spearrin, R. M., and Goldenstein, C. S. (2016) Spectroscopy and optical diagnostics for gases. Springer International Publishing, Switzerland.

Hugi A., Villares G., Blaser S., Liu H. C.: Mid-infrared frequency comb based on a quantum cascade laser, Nature 492, 229–233, 2012

Villares, G., Hugi, A., Blaser, S., Faist, J., Dual-comb spectroscopy based on quantum-cascadelaser frequency combsNat. Commun. 5, 5192, 2014

## **Catalytic Pyrolysis Kinetics of Polystyrene from WEEE**

Pereira P., Rey F., Rijo B., Carvalho T., Lemos F., Lemos M.A.N.D.A.<sup>\*</sup> CERENA, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

Keyword:	Kinetic	study,	Catalytic	pyrolysis,	Polystyrene,	WEEE	plastics,	zeolite

Electric and electronic equipment waste (WEEE) is one of the fastest growing waste streams in the world with 44.7 million ton generated in 2016, 30% being plastics. The European recycling industry recycles over 50 % of WEEE into Post-Consumer Recycled plastics, while the rest is mainly incinerated. The challenges for recycling are: difficult separation of the materials, presence of additives and legal constraints (EERA 2017). Tertiary recycling, particularly catalytic pyrolysis, is able to convert mixed and unwashed plastic waste into more valuable chemicals or fuels (Aguado et al. 2008). Knowledge of pyrolysis kinetics is of paramount importance for process design. This study focuses on the kinetics of the catalytic pyrolysis of WEEE (before and after a thermal pre-treatment used for ulterior plastic separation). Several acid catalysts - HZSM-5, H $\beta$ , HY and LZ-Y82 – were used. The kinetics was investigated using a simultaneous TG/DSC apparatus and a bench scale reactor. The results were compared with the ones obtained with virgin plastics. The presence of a catalyst induces a lower temperature degradation, visible in a broad peak in the TG curves. Several kinetic schemes were tested for all the catalysts. The activation energy was estimated from the best fitting model (fig. 1b) and compared for the different catalysts under testing.



Figure 1. Pyrolysis of WEEE PS with different acid catalysts (a) and DTG comparison between model and experimental data (b).

#### Acknowledgments

The authors thank FCT for financial support through CERENA (project UID/ECI/04028/2019) and project PTDC/EQU-EQU/29614/2017. Also, to Ambigroup, for the WEEE samples.

#### References

Aguado J Serrano DP, Escola JM. Fuels from Waste Plastics by Thermal and Catalytic Processes: A Review Ind Eng Chem Res 2008; 47: 7982-7992. EERA. 2017. "EERA' s Comments and Proposals for the EU Plastics Strategy 2017

## Experimental and kinetic modeling investigation on laminar flame propagation of engine fuels in a high-pressure constant-volume cylindrical combustion vessel

Yuyang Li<sup>\*</sup>, Bowen Mei, Xiaoyuan Zhang, Wei Li, Siyuan Ma, Guoqing Wang, Wenhao Yuan School of Mechanical Engineering, Shanghai Jiao Tong University, Shanghai 200240, P.R. China

#### Keywords

Engine fuels, laminar flame propagation, combustion vessel, high pressures, kinetic model.

Laminar flame propagation studies provide not only useful information about fuel properties, but also key validation targets for kinetic models. In this work, a high-pressure constant-volume cylindrical combustion vessel was designed to ensure the investigation of laminar flame propagation and instabilities over 298-500 K, 1-20 atm and a wide range of equivalence ratios for engine fuels (Wang et al., 2017). A dual-direction-protection and self-sealing strategy was proposed to avoid quartz window damage and leakage at the static pressure up to 200 atm. Schlieren method with a high speed camera was applied to record the flame images. The nonlinear extrapolation method proposed by Kelley and Law was applied to obtain the laminar burning velocity (LBV). With this new apparatus, the laminar flame propagation of gaseous fuels, low boiling point liquid fuels, as well as high boiling point liquid fuels, such as aromatic fuels (benzene, toluene, ethylbenzene, n-propylbenzene), cycloalkane fuels (decalin), alkanes (n-heptane), alkenes (1-hexene and 1-heptene), alcohols (methanol, propanol isomers and butanol isomers) and nitrogenous fuels (ammonia), has been investigated under elevated pressures (Li et al., 2018; Wang et al., 2017&2018; Zhang et al., 2017). Experimental observations demonstrated a variety of novel phenomena regarding to flame instabilities. For example, pulsating instabilities were observed for high-boiling point fuels, as reported in an *n*-butanol/O<sub>2</sub>/He flame at 20 atm. The cellular instability was found to increase from lean to moderate rich conditions, while the instability was found to decrease after the equivalence ratio is larger than 1.4. On the other hand, LBVs and Markstein lengths of the aforementioned fuels were obtained. Apparent fuel structural effects have been observed on the measured LBVs. Kinetic models of these fuels were developed and validated against extended conditions of laminar flame propagation. Key radical reactions related to fuel specific chemistry were found to play important roles in the observed fuel structural effects on LBVs. For example, the LBVs of benzene, toluene and ethylbenzene demonstrate strong thermodynamic and kinetic effects, which can be attributed to the different C/H ratios of fuels and the ability to form benzyl radical. The LBVs of *n*- and *i*-propanol demonstrate strong fuel isomeric effect, which can be attributed to the abilities of the isomeric fuels to produce reactive radicals (formyl, vinyl and ethyl) or stable radicals (methyl and allyl).

#### References

Li W, Wang GQ, Li YY, Li TY, Zhang Y, Cao CC, Zou JB, Law CK, Experimental and kinetic modeling investigation on pyrolysis and combustion of n-butane and i-butane at various pressures, Combust. Flame 2018;191:126-141.

Zhang XY, Wang GQ, Zou JB, Li YY, Li W, Li TY, Jin HF, Zhou ZY, Lee Y-Y. Investigation on the oxidation chemistry of methanol in laminar premixed flames. Combust Flame 2017;180:20-31.

Wang GQ, Li YY, Yuan WH, Zhou ZB, Wang Y, Wang ZZ. Investigation on laminar burning velocities of benzene, toluene and ethylbenzene up to 20 atm. Combust Flame 2017;184:312-323.

Wang GQ, Li YY, Yuan WH, Wang YZ, Zhou ZB, Liu YZ, Cai JH. Investigation on laminar flame propagation of n-butanol/air and n-butanol/O<sub>2</sub>/He mixtures at pressures up to 20 atm, Combust Flame 2018;191:368-380.

\*Corresponding author: yuygli@sjtu.edu.cn.

## FORMATION KINETICS OF WATER-SOLUBLE LANTHANIDE(III) PORPHYRINS AS POTENTIAL BIOMEDICAL AGENTS

Zsolt Valicsek<sup>\*</sup>, Melitta Patrícia Kiss and Ottó Horváth Department of General and Inorganic Chemistry, Institute of Chemistry, Faculty of Engineering, University of Pannonia, P.O.B. 158, H-8201 Veszprém, Hungary

#### Keywords

simultaneous metal and ligand control, out-of-plane metalloporphyrins, lanthanide(III) ions, tail-to-tail oligomerization.

Lanthanide(III) ions are advantageous in the researches focusing on the special features of outof-plane metalloporphyrins, owing to the lanthanide contraction. The mechanism of their insertion into the coordination cavity of a porphyrin ligand is complicated in water, as a consequence of their stable aqua complexes and oligomer forms. Lanthanide(III) ions, possessing Pearson-type hard character, can connect rather to the peripheral substituents of porphyrin if they contain similarly hard O-donor groups (e.g., carboxy-, sulfonato-phenyl). Only under thermodynamic control, at higher temperatures, can insert the metal ion into the cavity of the porphyrin.

Moreover, they incline to higher coordination number (8–12), which is manifested in their sandwich complexes, owing to the simultaneous coordination of two tetradentate porphyrin ligands to a metal center. Generally, such type of lanthanide(III) porphyrin complexes are applied for medical purposes as MRI contrast agents, for NIR emission, photodynamic diagnosis (PDD), and therapy (PDT).

We have started a systematic research work with the early lanthanide(III) ions of even atomic numbers ( $_{58}$ Ce,  $_{60}$ Nd,  $_{62}$ Sm, and  $_{64}$ Gd). In this project, the kinetics of their insertion into the cavity of an anionic, 5,10,15,20-tetrakis(4-sulfonatophenyl) porphyrin was investigated.

This work was supported by the Széchenyi 2020 under the GINOP-2.3.2-15-2016-00016.

#### References

Imran M, Kiss MP, Valicsek Z, Horváth O. Formation, photophysics and photochemistry of anionic lanthanide(III) mono- and bisporphyrins. Molecules 2019;24:1309-1322.

Horváth O, Valicsek Z, Fodor MA, Major MM, Imran M, Grampp G, Wankmüller A. Visible light-driven photophysics and photochemistry of water-soluble metalloporphyrins. Coord. Chem. Rev. 2016;325:59–66.

## LAMINAR BURNING VELOCITIES AND LIF MEASUREMENTS OF NITRIC OXIDE FORMATION IN FLAMES OF SIMPLE ALCOHOLS

C. Brackmann, T. Methling, G. Capriolo, M. Lubrano Lavadera, A.A. Konnov<sup>\*</sup> Combustion Physics, Lund University, Box 118, SE-221 00 Lund, SWEDEN

Keywords

Methanol, Ethanol, Propanol, Burning velocity, Nitric oxide.

The use of short aliphatic alcohols as additives to transportation fuels has been proven to sensibly reduce harmful pollutants, such as CO, HC and soot, while some inconsistencies among different studies were observed for nitric oxide (NO) emissions. To this end, it would be of particular interest to analyze the effect of alcohol structure on NO formation. In this study, the laser-induced fluorescence (LIF) technique was applied to measure quantitative NO concentration in the product zone of premixed flames of alcohols and air. Flames were stabilized on a heat-flux burner at 1 atm over the equivalence ratio range 0.7-1.4. The heat flux method yields laminar burning velocities and ensures a steady 1D structure of the flames. The laser power used resulted in fluorescence measurements in the so-called saturated regime to minimize quenching effects. Measurements were performed in the production zone at 10 mm above the burner plate.

The method was verified by the measurements of NO concentration in premixed methane+air flames for which results could be compared with previous LIF and probe-sampling measurements. Methanol+air flames were stabilized at initial gas temperature of 318 K. Methane and methanol flames were modelled using five kinetic mechanisms from literature. While the thermal NO is well predicted by all the models, there is large variation between predictions of the prompt NO formation.

New accurate measurements of the adiabatic laminar burning velocities and NO concentrations of ethanol, n-heptane and a mixture of them at initial gas temperature of 338 K are also reported. The results demonstrate similar trends as a function of equivalence ratio for the investigated fuels. The ethanol+air mixture shows higher burning velocities and lower NO concentrations than the other two mixtures. The burning velocities of these flames are accurately reproduced by the PoliMi detailed kinetic mechanism, however model predictions significantly deviate from the experiments for the prompt NO formation in rich flames.

Burning velocity of the flames of propanol isomers were measured at initial gas temperature of 323 K. N-propanol has notably higher burning velocity than i-propanol, however, no appreciable differences were observed between the two isomers for the NO formation over entire range of equivalence ratios. A new detailed kinetic mechanism for propyl alcohols combustion is presented, and numerical simulations showed good agreement with experimental data both for the burning velocities and NO concentrations. These series of measurements are believed to be valuable data for validation of detailed kinetic models.

## Chemistry triggered events of PM<sub>2.5</sub> explosive growth during late autumn and winter in a megacity

Wenwen Sun<sup>1</sup>, Dongfang Wang<sup>2</sup>, Lan Yao<sup>3</sup>, Qingyan Fu<sup>2</sup>, Hongli Wang<sup>3</sup>, Qing Li<sup>1</sup>, Gehui Wange<sup>3</sup>, Jianmin Chen<sup>1, 3</sup>.\*

<sup>1</sup> Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention, Department of Environmental Science & Engineering, Institute of Atmospheric Sciences, Fudan University, Shanghai 200438, China

<sup>2</sup> Shanghai Academy of Environmental Sciences, Shanghai 200233, China <sup>3</sup> Institute of Eco-Chongming, 3663 Zhongshan Road, Shanghai 200062, China

To better understand the formation of PM<sub>2.5</sub> explosive growth (EG) events, we synchronously monitored the online hourly-resolution mass concentration, water-soluble ions, organic carbon, and element carbon of PM<sub>2.5</sub>, and recorded gaseous pollutants and meteorological factors in late autumn and winter in Shanghai between 2014 and 2017. Here, EG is defined as the net increase of mass concentration of PM<sub>2.5</sub> more than 100  $\mu$ g m<sup>-3</sup> in 3, 6, or 9 h, respectively. Our results reveal that the total EG events gradually decreased from 19 times in 2014 to 6 times in 2017, and the mean annual level of PM<sub>2.5</sub> decreased from 183.6 to 128.8 µg m<sup>-3</sup> in the same period. The potential source contribution function (PSCF) shows that 45% (230 h, 163.0 µg m<sup>-3</sup>) of the EG events originated from the local area and 55% (198 h, 156.9 µg m<sup>-3</sup>) came mainly from the North China Plain. Under stagnant conditions, the major components contributing to PM<sub>2.5</sub> were NO<sub>3</sub>- (17.9%), OM (14.1%),  $SO_4^{2-}(13.1\%)$  and  $NH_4^{+}(13.1\%)$ . The driving factors of EG events under stagnant conditions were secondary aerosol formation (NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup>) and primary emissions (vehicle emission, fireworks and biomass burning). Sulfate and nitrate formation are significantly related to relative humidity (RH) and dominated by gas-phase oxidation and heterogeneous reactions. These results enhance our understanding of the major driving factors of EG and they provide a basis for policymakers to control air pollution in Shanghai.

#### Keywords

*PM*<sub>2.5</sub> *explosive growth; PSCF; gas-phase oxidation; heterogeneous reaction* 

#### References

Fu, H., Chen, J., 2017. Formation, features and controlling strategies of severe haze-fog pollutions in China. Sci. Total. Environ. 578, 121-138.

George, C., Ammann, M., D'Anna, B., Donaldson, D., Nizkorodov, S., 2015. Heterogeneous photochemistry in the atmosphere. Chem. Rev. 115, 4218-4258.

## A Kinetic View on Dissociative Electron Attachment Processes

J. Troe<sup>1,</sup> Albert A. Viggiano<sup>2</sup>

<sup>1</sup> Max-Planck-Institut f
ür biophysikalische Chemie, Am Fassberg 11, D-37077 G
öttingen, Germany
 <sup>2</sup> Air Force Research Laboratory, Space Vehicles Directorate, 3550 Aberdeen Avenue SE, Bldg 570, Kirtland Air Force Base, New Mexico 87117-5-776, USA

Keywords

Electron attachment and detachment processes

Nondissociative (NDEA) and dissociative electron attachment (DEA) as well as the reverse electron autodetachment and dissociation processes of the created anions play an important role in plasmachemical kinetics. It appears, therefore, desirable to integrate these processes into the formalism of chemical kinetics.

In the presence of collisions stabilizing the formed anions, falloff curves of NDEA are constructed (Troe et al., 2007). In DEA experiments, the anions initially are produced at high internal energies, before they relax toward thermal equilibrium distributions (Viggiano et al., 2007). In this stage, DEA behaves like a "chemical activation" or "complex-forming bimolecular reaction" system. After equilibrium distributions are reached, DEA continues as a two-channel thermal dissociation reaction (Troe, 2019). Analyzing the competition between the two channels (autodetachment of electrons and anion fragmentation), it is shown that the former effectively behaves as a rigid-activated complex process, whereas the latter corresponds to a loose activated complex (AC). The competition then is governed by the energetics of the channels, but angular momentum - effects also play an important role. They give rise to "rotational channel switching": if the dissociation is energetically less favorable in the absence of rotations, the rigid-AC/loose-AC character of the system may invert the energetic order of the channel threshold energies in the presence of rotations. This may make dissociation more favorable than autodetachment in rotating anions. The effect strongly influences the pressure dependence of the fragmentation yields of DEA.

#### References

Troe J, Miller TM, Viggiano AA. Low-energy electron attachment to SF6. I. Kinetic modelling of nondissociative electron attachment. J Chem Phys 2007; 127:244303.

Troe J. Simplified analysis and representation of multichannel thermal unimolecular reactions. J Phys Chem A 2019; 123: 1007 - 1014.

Viggiano AA, Miller TM, Friedman JF, Troe J. Low-energy electron attachment to SF6. III. From thermal detachment to the electron affinity of SF6. J Chem Phys 2007; 127: 244305.

## Rate constant measurements and RRKM modeling on thermal decomposition of ethylsilanes and cyclosiloxanes

S. Peukert<sup>1\*</sup>, P. Sela<sup>1</sup>, Y. Sakai<sup>2</sup>, J. Herzler<sup>1</sup>, M. Fikri<sup>1</sup>, and C. Schulz<sup>1</sup>

<sup>1</sup>Institute for Combustion and Gas Dynamics – Reactive Fluids and CENIDE, Center for

Nanointegration, University of Duisburg-Essen, Duisburg, Germany

<sup>2</sup>Graduate School of Engineering, University of Fukui, Fukui, Japan

#### Keywords

Silicon-organic precursors, shock tube, RRKM modeling, structure-activity relationships

Monoethylsilane ( $H_3Si(C_2H_5)$ ; ES) and diethylsilane ( $H_2Si(C_2H_5)_2$ ; DES) are homologs in the group of alkylsilanes, whereas hexamethyl-cyclotrisiloxane (cyc-Si<sub>3</sub>O<sub>3</sub>(CH<sub>3</sub>)<sub>6</sub>; D3) and octamethyl-cyclotetrasiloxane (cyc-Si<sub>4</sub>O<sub>4</sub>(CH<sub>3</sub>)<sub>8</sub>; D4) are important representatives of cyclic siloxanes. All these compounds are used as precursors for the production of Si-containing nanoparticles and thin films by spray-flame synthesis or chemical vapor deposition (CVD). The gas-phase decomposition of these precursors was studied in a shock tube in a temperature range of 1030–1550 K and at pressures ranging from 1.5 to 2.5 bar behind reflected shock waves using gas chromatography/mass spectrometry (GC/MS) and high-repetition-rate time-of-flight mass spectrometry (HRR-TOF-MS). In case of ES and DES, GC/MS and HRR-TOF-MS measurements were complemented by H-ARAS (Atomic Resonance Absorption Spectrometry) (at 1230–1500 K;  $p \approx 1.4$  bar). In addition to the experiments, quantum-chemical calculations using the G4MP2 composite method clearly indicate that the initial unimolecular reaction step in both ES and DES is H<sub>2</sub> elimination. Regarding ES, this finding is in agreement with results from a previous shock tube study reported by Rickborn et al. (1984). In case of D3 and D4, the initial decomposition step was suggested to proceed by an elimination of dimethylsiloxane (SiCH<sub>3</sub>)<sub>2</sub>O; D1) (Almond et al., 2008). Electronic structure calculations at the B3LYP/6-311+g(2d,2p) level of theory suggest that the initial decomposition reactions of D3 and D4 proceed by the elimination of an enol ((CH<sub>3</sub>)SiCH<sub>2</sub>(OH)) via a four-centered transition state. Measured rate constants for ES, DES, D3, and D4 decomposition were complemented by RRKM calculations. The experimental and theoretical data from this work are compared with previous results from our laboratory on the pyrolysis of tetramethylsilane (Si(CH<sub>3</sub>)<sub>4</sub>; TMS) and tetramethoxysilane (Si(OCH<sub>3</sub>)<sub>4</sub>; TMOS) (Sela et al. 2018 and 2019) and an outlook for structure-activity relationships of initial unimolecular reactions of silicon organic compounds with variable ligands will be given.

#### References

Almond MJ, Becerra R, Bowes SJ, Cannady JP, Ogden JS, Walsh R. A mechanistic study of cyclic siloxane pyrolyses at low pressures. Phys Chem Chem Phys 2008;10:6856-6861.

Rickborn SF, Ring MA, O'Neal HE. The kinetics and mechanism of the shock induced gas phase decomposition of ethylsilane. Int J Chem Kinet 1984;16:1371-1383.

Sela P, Peukert S, Herzler J, Fikri M, Schulz C. Shock-tube study of the decomposition of tetramethylsilane using gas chromatography and high-repetition-rate time-of-flight mass spectrometry. Phys Chem Chem Phys 2018;20:10686-10696.

Sela P, Peukert S, Herzler J, Sakai Y, Fikri M, Schulz C. High-temperature gas-phase kinetics of the thermal decomposition of tetramethoxysilane. Proc Combust Inst 2019;37:1133-1141.

## Understanding Temperature and Pressure Dependence in the Non Adiabatic Reactions of Oxygen Atoms with Terminal Alkenes

Carlo Cavallotti,<sup>1\*</sup>Luna Pratali Maffei<sup>1</sup>, Adriana Caracciolo<sup>2</sup>, Nadia Balucani<sup>2</sup> and Piergiorgio Casavecchia<sup>2</sup>

<sup>1</sup>Department of Chemistry Materials and Chemical Engineering, Politecnico di Milano, Piazza Leonardo da Vinci 33, 20133, Milan, ITALY

<sup>2</sup>Laboratory of Molecular Processes in Combustion, Department of Chemistry, Biology and Biotechnologies, University of Perugia, 06123 Perugia, ITALY

#### Keywords

Reactive Scattering, Crossed Molecular Beams,  $O({}^{3}P)+Alkene$  Reactions, Intersystem Crossing, Rate Laws

The reactions of ground state atomic oxygen  $O(^{3}P)$  with olefins have been extensively studied for more than sixty years in atmospheric chemistry. Recently, it was shown that their total rate coefficients exhibit a significant non-Arrhenius temperature dependence, which suggests that the reaction of O(<sup>3</sup>P) with olefins is important also in astrochemical kinetics (Sabbah et al. 2007). It is also well known that the reactions of atomic oxygen can influence significantly the reactivity in the early stages of hydrocarbon combustion. Unfortunately, while the global reaction rate for many members of this reaction class is well established, much less is known about their channel specific reactivity. The reasons for this are several. First, the reactivity is very rich. Secondly, several reaction channels are accessed only after intersystem crossing (ISC) from the triplet to the singlet potential energy surface (PES), which poses a considerable theoretical challenge to the accurate determination of reaction rates. Thirdly, many of the reaction products are radicals and thus reactive species, and therefore it is quite difficult experimentally to discriminate the primary from the secondary reactivity. Recently, we combined crossed-molecular-spectrometric detection and time-of-flight (TOF) analysis to high-level ab initio electronic structure calculations of the triplet/singlet PESs and RRKM/Master Equation computations of BRs including ISC to investigate the reaction between O(<sup>3</sup>P) and several unsaturated hydrocarbon (Cavallotti et al 2014, Vannuzzo et al. 2016). Here, we extend the same approach to study the  $O({}^{3}P)+1$ -butene reaction. The analysis of this system allows to formulate for the first time rate rules and predict the reactivity of the whole O(<sup>3</sup>P)+terminal alkenes reaction class across wide temperature and pressure ranges. It is found that the extent of ISC increases with the molecular size, that at the low temperatures of interstellar space the reactivity is governed by ISC and decomposition to radicals, while in atmospheric conditions collisional stabilization is dominant. In combustion environments the main reaction channels, H<sub>2</sub>CO formation, H displacement, and H abstraction, are on the triplet PES.

#### References

Sabbah H, Biennier L, Sims, IR, Georgievskii, Y, Klippenstein, SJ, Smith, IWM Science 2007; 317; 102-105.

Cavallotti C, Leonori F, Balucani N, Nevrly V, Bergeat A, Falcinelli S, Vanuzzo G, Casavecchia, P J. Phys. Chem. Lett. 2014; 5; 4213-4218.

Vanuzzo G, Balucani N, Leonori F, Stranges D, Casavecchia P, Gimondi I, Cavallotti C, J. Phys. Chem. Lett. 2016; 7; 1010.

\*Corresponding author: carlo.cavallotti@polimi.it

## IMPACT OF CORRELATED INPUTS ON COMPUTED BRANCHING RATIO

Can Huang<sup>1,2</sup>, Zijun Zhou<sup>2</sup>, Bin Yang<sup>2</sup> and Feng Zhang<sup>1,\*</sup>

<sup>1</sup> National Synchrotron Radiation Laboratory, University of Science and Technology of China,

Hefei, Anhui, 230029, P. R. China

<sup>2</sup> Center for Combustion Energy and Key Laboratory for Thermal Science and Power Engineering of MOE, Tsinghua University, Beijing, 100084, P. R. China

Keywords

Branching ratio, Uncertainty quantification, RRKM/master equation, Transition state theory, Correlation

The product branching ratio between competing reaction pathways is as important as the absolute rate constant, in terms of both understanding the fundamental mechanisms of reaction systems and the optimization of detailed models (Manion and Mcgivern, 2016). While experiments could provide accurate product ratios (Awan et al., 2012), less attention has been given to quantitatively evaluate the uncertainty of the theoretically calculated ratios, especially on how the correlation of input uncertainties propagates to these relative rates. In the present work, uncertainty analysis was performed on the branching ratio of two typical competing reaction systems: the site-specific reactions (H abstraction reaction) that are calculated by transition state theory and the multi-well & multi-channel reactions that are calculated by RRKM/master equation. By comparing two scenarios that with and without considering the correlation among the input molecular parameters, we found that the inclusion of input correlation would dramatically reduce the uncertainty of the predicted branching ratio. For site-specific reactions, the inclusion of the correlation of energy parameters is the key factor in reducing the branching ratio. However, for the multi-well & multi-channel reactions is significant for the collisional and reactant parameters, even in the scenario that input correlation is not included.



Fig.1 (left) Histograms of the sampled relative ratios of  $k_{W6=P2}$  and  $k_{W6=P3}$ ; (right) Global uncertainties for the absolute rate constants of W6 = P2 and W6 = P3 together with their relative ratio.

#### References

Awan, I. A.; Burgess, D. R. Jr.; Tsang, W.; Manion, J. A. Standard reactions for comparative rate studies: Experiments on the dehydrochlorination reactions of 2- chloropropane, chlorocyclopentane, and chlorocyclohexane. Int. J Chem. Kinet. 2012; 44, 351–368.

Manion J A, McGivern W S. The importance of relative reaction rates in the optimization of detailed kinetic models. Int. J Chem. Kinet. 2016; 48(7): 358-366.

\*Corresponding author: feng2011@ustc.edu.cn

## NEW PHENOMENOLOGICAL REACTION RATE EQUATION FOR CHEMICAL CATALYST DEACTIVATION

Z. J. G. Gromotka \*1, G. S. Yablonsky<sup>2</sup>, G. B. Marin<sup>3</sup> and D. Constales<sup>1</sup>

 <sup>1</sup>Department of Mathematical Analysis, Ghent University, Krijgslaan 281, B9000 Ghent, Belgium
 <sup>2</sup>Department of Energy, Environmental and Chemical Engineering, McKelvey School of Engineering, Washington University in St. Louis, Campus Box 1180, St. Louis MO 63130, USA
 <sup>3</sup>Laboratory for Chemical Technology, Ghent University, Technologiepark 914, B9052 Ghent,

Belgium

Keywords Aging, Analytic model, Catalyst, Deactivation, Irreversible, Reaction rate, Reversible.

Catalyst deactivation is the complex non-steady-state process which is governed by many physico-chemical factors reflecting a variety of phenomena, i.e. chemical deactivation, fouling, thermal and mechanical degradation (Argyle and Bartholomew, 2015). In this paper, a new phenomenological reaction rate equation is presented for the typical heterogeneous catalytic reaction accompanied by reversible deactivation and aging (irreversible deactivation). The equation based on linear mechanism and mass-action-law assumptions is characterized by the 'separable' form:  $R(t) = R_{qss}\psi_{d,r}v_{d,ir}N_T$ , where R and  $R_{qss}$  are the reaction rate and quasi-steady-state rate for the main route, respectively;  $\psi_{d,r}$ ,  $\psi_{d,ir}$  are factors of reversible and irreversible deactivation, respectively;  $N_T$  is the total number of active sites. The result is a further development of the approach proposed by Ostrovskii and Yablonsky (1989). For the typical two-step catalytic mechanism  $(1.A + K \longrightarrow AK; 2. AK \longrightarrow B + K)$  accompanied by reversible deactivation (3.  $AK \xleftarrow{k_3}{k_4} X)$  and irreversible deactivation (4.  $X \xrightarrow{k_5} Y$ ).  $k_1$ ,  $k_2$ ,  $k_3$ ,  $k_4$  and  $k_5$  are apparent kinetic coefficients which in general include concentrations of reactants or/ and products as factors. Typically,  $k_1$ ,  $k_2 \gg k_3$ ,  $k_4 > k_5$ . In this case  $R_{qss} = \frac{k_1k_2}{k_1+k_2}$ ;  $\psi_{d,r} = \frac{k_4}{\alpha k_3+k_4} + \frac{\alpha k_3}{\alpha k_3+k_4} e^{-(\alpha k_3+k_4)t}$ ;  $\psi_{d,ir} = \exp\left[-\frac{\alpha k_3 k_5}{\alpha k_3+k_4}t - \frac{\alpha k_3 k_5}{(\alpha k_3+k_4)^2}(e^{-(\alpha k_3+k_4)t} - 1)\right]$ .  $\alpha \equiv C_{qss,AK} = \frac{k_1}{k_1+k_2}$ , is the quasi-steady-state concentration of the catalytic intermediate AK; the factor  $\psi_{d,r}$  is a function of both its own kinetic parameters (reversible deactivation) and the parameters of the main reaction; the factor  $\psi_{d,ir}$  factor is a function of all kinetic parameters. The obtained equation was studied analytically and computationally; it was illustrated by analysis of deactivation of reforming processes.

#### References

Argyle MD, Bartholomew CH, Heterogeneous catalyst deactivation and regeneration: a review, Catalyst, 2015;5(1):195-269.

Ostrovskii NM, Yablonsky GS, Kinetic equation for catalyst deactivation, React. Kinet. Catal, Lett, 1989;39(2):287-292.

<sup>\*</sup>Corresponding author: Zoe.Gromotka@UGent.be

## Determination of bond additivity corrections for CBS-QB3 calculated standard enthalpies of formation of C, H, N, O and S species

Cato A.R. Pappijn<sup>1</sup>, Ruben Van de Vijver<sup>1</sup>, Florence Vermeire<sup>1</sup>, Marie-Françoise Reyniers<sup>1</sup>, Guy B. Marin<sup>1</sup> and Kevin M. Van Geem<sup>1,\*</sup>

<sup>1</sup>Laboratory for Chemical Technology, Ghent University, Technologiepark 121, 9052 Zwijnaarde, Belgium

Keywords

Quantum chemistry, thermodynamic properties, bond additivity corrections.

A prerequisite for the generation of detailed fundamental kinetic models is the availability of accurate thermodynamic data. To address the scarcity of reliable experimental data, theoretical calculations and approximation methods based on these calculations are typically used. The accuracy of the quantum chemistry method for determination of thermodynamic properties can be improved by using empirical correction methods, such as the isodesmic "Bond additivity correction method" (BACs), as introduced by Petersson et al. (1998). Usually, BACs are determined for several bond types via least-squares regression using a database of reliable experimental standard enthalpies of formation. In previous work (e.g. Ince et al., 2015), BACs have been determined for the CBS-QB3 method from small experimental databases for certain classes of molecules. Using the newly developed algorithm for automatic assignment and regression, a set of BACs has been determined from an experimental database of 145 molecules, containing both non-cyclic and cyclic species and consisting of the elements C, H, N, O and S. The mean absolute error between experimental and ab initio enthalpies of formation at 298.15 K decreases from 5.6 to 2.1 kJ mol<sup>-1</sup> when using the calculated BACs (Figure 1).



Figure 1: Absolute difference between the experimental and the CBS-QB3 (with and without BAC correction) standard enthalpy of formation ( $\Delta_f H^{\circ}$ ) at 298.15 K for 5 different molecules consisting of C, H, N, O and S (left) and for all the species included in the dataset (right).

#### References

Petersson GA., Malick D, Wilson W, Ochterski JW, Montgomery JA, Frisch MJ, J Chem Phys 1998;109(24):2598-2619

Ince A, Carstensen H-H, Reyniers M-F, Marin GB., AIChE J 2015;61:3858-3870

\*Corresponding author: Kevin.VanGeem@UGent.be

## ELECTRODE KINETICS OF STRONGLY ADSORBED MOLECULES ON SEMICONDUCTORS: ISOLATING KINETIC CONSTANTS FROM LATERAL INTERACTIONS AND DIODE PARAMETERS

Simone Ciampi<sup>1,\*</sup>, Yan B. Vogel<sup>1</sup> Angela Molina<sup>2</sup> and Joaquin Gonzalez<sup>2</sup> <sup>1</sup>Curtin Institute of Functional Molecules and Interfaces, Curtin University, Bentley, Western Australia 6102, AUSTRALIA <sup>2</sup>Departamento de Quimica Fisica, Universidad de Murcia, Murcia 30003, SPAIN

Keywords: Electrode kinetics, semiconductors, strongly adsorbed molecules, votlammetry

Where there is the need to gain insights on charge transfer kinetics, either in energy conversion, catalysis or molecular electronics, then the scientist or the engineer require an analytical tool for the measurement (Laviron, 1979). In this context, voltammetry still reigns supreme. Then, in order to translate experimental numbers into quantitative insights on the "speed" of charge transfer, any given electrochemical measurement needs to be coupled to a theoretical model (Santangelo, 1988). Cyclic voltammetry is by far the prime and most widely-used form of electrochemical spectroscopy (i.e. simple, ubiquitous and informative). Current theoretical models for the analysis of voltammetry fall short of capturing all of the factors at play, and most notably, they do not account for electrostatics (Vogel et al., 2017). For semiconductors, and to a degree also for metals, the reproducibility of published kinetic data is extremely poor and we believe a big contributor to this problem is the naïve character of common models for kinetics. The purpose of this talk is to describe step-by-step analytical procedure to simulate current-potential traces of cyclic voltammograms for electroactive species adsorbed on semiconductor electrodes, allowing to retrieve kinetic and diode parameters from the fitting of experimental data. This model also allows accounting for i) changes in photocurrents (i.e. open circuit values) between forward and backward sweeps, and ii) attractive and repulsive intermolecular forces sensed by the monolayer. By using this model, we have obtained quantitative insights on the kinetics of a ferrocene monolayer tethered on amorphous silicon photoanodes and photocathodes. From electrocatalysis to molecular electronics, this dynamic electrostatic landscape is always part of the system under investigation. It can be a "friend or a foe", but either way it needs to be accounted for when studying electrode kinetics. This aspect was long neglected.

#### References

Laviron, E. General Expression of the Linear Potential Sweep Voltammogram in the Case of Diffusionless Electrochemical Systems. J. Electroanal. Chem. Interfacial Electrochem. 1979; 101:19-28.

Santangelo, P. G.; Miskelly, G. M.; Lewis, N. S. Cyclic Voltammetry at Semiconductor Photoelectrodes. 1. Ideal Surface-Attached Redox Couples with Ideal Semiconductor Behavior. J. Phys. Chem. 1988; 92:6359-6367.

Vogel, Y. B.; Zhang, L.; Darwish, N.; Gonçales, V. R.; Le Brun, A.; Gooding, J. J.; Molina, A.; Wallace, G. G.; Coote, M. L.; Gonzalez, J.; Ciampi, S. Reproducible Flaws Unveil Electrostatic Aspects of Semiconductor Electrochemistry. Nat. Commun. 2017; 8:2066.

\*Corresponding author: simone.ciampi@curtin.edu.au

## **On the Combustion Chemistry of Alkyl Nitrates**

C. Franklin Goldsmith \*1, Mark E. Fuller<sup>1</sup> and Nabiha Chaumeix<sup>2</sup>

<sup>1</sup>School of Engineering, Brown University, Providence, RI, USA

<sup>2</sup>CNRS-INSIS, Institut de Combustion, Aérothermique, Réactivité et Environnement 1C, Avenue de la recherche scientifique, 45071 Orléans cedex 2, FRANCE

*Keywords alkyl nitrates, nitrogen chemistry, laminar flame speeds, ignition delays* 

This talk will summarize our recent efforts to understand the kinetics of alkyl nitrates as fuel additives. The work is a collaborative effort between Brown University and the CNRS-Orléans. The majority of the talk will focus on isopropyl-nitrate (iPN) as a surrogate for larger nitrates. The dissociation and pyrolysis of iPN was characterized using shock tube laser schlieren densitometry. A corresponding RRKM/Master Equation was developed to provide accurate extrapolations to higher pressures and temperatures. Laminar flame speeds of iPN/O<sub>2</sub> mixtures were performed at 0.5 and 1.0 bar. Ignition delay measurements were performed at a nominal reflected shock pressure of 20 bar, for C<sub>3</sub>H<sub>8</sub> / O<sub>2</sub> blends at equivalence ratios of  $\phi = 0.5$ , 1.0, and 1.5, with iPN: C<sub>3</sub>H<sub>8</sub> ratios of 0.00, 0.01, and 0.10 to account for fuel-nitrate interactions in combustion. The work is accompanied by a new detailed chemical kinetic mechanism. The results are summarized in the figures below, with the flame speeds on the left and ignition delays on the right. Broadly speaking, the mechanism is in excellent agreement with the measured data. For the flame speeds, the biggest discrepancies are at the extreme fuel-rich end; for the ignition delays, the mechanism fails to capture the low-temperature chemistry for 10% iPN at  $\phi = 1.0$ .



Figure 1: Summary of results for iPN combustion kinetics. The pane on the left is the laminar burning velocity of iPN. The three panes to the right are the ignition delay times of propane/iPN blends at three different equivalence ratios. The symbols are the experimental results, and the lines are the model predictions.

<sup>\*</sup>Corresponding author: franklin\_goldsmith@brown.edu

## COMPARATIVE METHODS OF KINETIC ANALYSIS OF CALCIUM LOOPING FOR ENERGY STORAGE

Larissa Fedunik<sup>1,2,\*</sup>, Alicia Bayon<sup>2</sup>, Wojciech Lipiński<sup>3</sup> and Scott W. Donne<sup>1</sup> <sup>1</sup>Discipline of Chemistry, University of Newcastle, Callaghan, NSW 2308, AUSTRALIA <sup>2</sup>CSIRO Energy, P.O. Box 330, Newcastle, NSW 2300, AUSTRALIA <sup>3</sup>Research School of Electrical, Energy and Materials Engineering, The Australian National University, Canberra, ACT 2601, AUSTRALIA

Keywords

Thermochemical Energy Storage, Chemical Looping, Carbonates, Thermochemistry, Chemical Kinetics

The calcium looping cycle is an important process which can reduce greenhouse gases emissions into the atmosphere through a variety of applications, such as solar thermochemical energy storage (TCES). This work aims to comprehensively analyse the reaction kinetics of the process. The calcium looping cycle is based on a cyclic chemical process (Bayon et al., 2018). CaO produced in the solar-driven endothermic calcination reaction (1) is cycled to the exothermic carbonation reaction (2), from which thermal energy is released to drive a power cycle.

$$CaCO_{3} \rightarrow CaO + CO_{2}(\Delta H_{r} > 0) \tag{1}$$

$$CaO + CO_2 \rightarrow CaCO_3(\Delta H_r < 0) \tag{2}$$

In this work, cycling reactions are performed using thermogravimetric analysis. In order to achieve scale-up of the calcium looping cycle, it is essential to calculate kinetic parameters (activation energies and reaction rates) of both calcination and carbonation. However, laboratory scale experiments of both experiments show a vast disparity in kinetic parameters, such as activation energies and reaction rates, depending on both the experimental atmosphere and the kinetic method used (Fedunik-Hofman, 2019).

In this work, we perform kinetic analyses of both calcination and carbonation using comprehensive techniques, including model-fitting methods (Coats-Redfern approach), model-free methods (isoconversional method) and semi-empirical methods ("apparent" models). The advantages and disadvantages of each method will be discussed, as well as potential reasons for the discrepancies in kinetic parameters obtained.

#### References

Bayon, A et al. Techno-economic assessment of solid–gas thermochemical energy storage systems for solar thermal power applications. Energy 2018;149:473-484.

Fedunik-Hofman, L et al. Friedman method kinetic analysis of CaO-based sorbent for high-temperature thermochemical energy storage. Chem Eng Sci 2019;200:236-247.

\*Corresponding author: larissa.fedunik-hofman@uon.edu.au

## PYROLYSIS MECHANISM AND KINETICS OF ISOPROPYL NITRATE

Mark E. Fuller<sup>1</sup> and C. Franklin Goldsmith<sup>\*1</sup>

<sup>1</sup>School of Engineering, Brown University, 184 Hope Street, Providence, RI 02906, USA

#### Keywords

shock tube, laser schlieren densitometry, isopropyl nitrate

The pyrolysis and decomposition of isopropyl nitrate dilute in both argon and krypton was investigated in a new shock tube facility with laser-schlieren densitometry. This new facility, developed by Fuller et al. (2019), employs a diaphragmless driver to generate shocks.

Experiments at pressures of 71, 126, and 240 Torr were conducted at temperatures between 700 and 1000 K. Initial predictions of the decomposition kinetics for isopropyl nitrate were developed with electronic structure theory and RRKM Master Equation methods and refined using the the experimental results. To improve the agreement between the experimental data and the modeling results, select parameters within the RRKM/ME were optimized. The bond dissociation energy (BDE), pre-factor for the energy transfer parameter,  $\langle \Delta E_{down} \rangle$ , and interaction potential coefficient,  $\alpha$ , were varied within ranges of reasonable uncertainty. The optimum parameter set was chosen to minimize the sum of square error between the log of the measured rate constants and the log of the RRKM/ME predictions.

The initial decomposition  $i-C_3H_7ONO_2 \rightleftharpoons i-C_3H_7O + NO_2$  has a high-pressure limit rate coefficient of  $5.70 \times 10^{22}T^{-1.80} \exp[-21287.5/T] s^{-1}$ . In modelling the experimental results, both a new chemical kinetic mechanism was developed as well as a new shock tube module was developed for CANTERA. The new shock tube module allows for arbitrarily large mechanisms in standard formats to be applied to the simulation of laser schlieren experiments, compared with the former modelling approaches.



#### References

Fuller, M.E., Skowron, M., Tranter, R.S., Goldsmith, C.F., 2019. A modular, multi-diagnostic, automated shock tube for gas-phase chemistry. Review of Scientific Instruments Submitted for review.

\*Corresponding author: franklin\_goldsmith@brown.edu

## First-Principles Calculation of Catalytic Activity Modifications with an Electric Field

Katsuhiro Wakamatsu<sup>1</sup> and Teppei Ogura<sup>1,\*</sup> <sup>1</sup>Kwansei Gakuin University, 2-1 Gakuen Sanda Hyogo, 669-1337 JAPAN

#### Keywords

Non-faradaic electrochemical modification of catalytic activity (NEMCA), Density functional theory, CO<sub>2</sub> methanation, Solid oxide electrolysis cell (SOEC), Hydrocarbon species, Electric field, Oxygen co-adsorption.

We must improve energy conversion efficiency in order to prevent the depletion of fossil fuels. Catalysis is used in most of the energy conversion technologies, so enhancement of catalytic activity is essential for improving energy efficiency. Non-Faradaic electrochemical modification of catalytic activity (NEMCA) by impression of an electric field (EF) is one of the methods to improve catalyst performance (e.g., Sekine et al., 2011). It has been discussed that oxygen anions forced electrochemically to adsorb on catalyst surface alter the catalyst electric property (Vayenas et al., 1988). However, given EF also changes the catalyst electric property directly. Because it is difficult to divide into these effects with an experimental approach, we have tried to theoretically investigate the mechanism of NEMCA in CO<sub>2</sub> methanation (CO<sub>2</sub> + 4H<sub>2</sub>  $\rightarrow$  CH<sub>4</sub> + 2H<sub>2</sub>O,  $\Delta H^{\circ}$  = -165 kJ/mol (1)) in solid oxide electrolysis cell (SOEC) (Atami et al., 2016) using the density functional theory (DFT). In concreate, we have focused on the rate-determining steps (RDSs) of CO<sub>2</sub> methanation proposed by our detailed surface reaction mechanism analysis. We have calculated the adsorption energies of hydrocarbon species related to RDSs on Ni(111) (CO<sub>2</sub>\* $\rightarrow$  CO\* + O\* (2), CHO\* $\rightarrow$  CH\* + O\* (3), CH<sub>3</sub>\* + H\* $\rightarrow$  CH<sub>4</sub> (4), \* means surface species) with an EF or co-adsorbed oxygen atoms.

In our calculative setup, when we evaluated the effect of an EF, used is thin film condenser model where the slab model is sandwiched between two condenser boards connected to the outlet electrode set with EF of  $\pm 0.25$ ,  $\pm 0.5$  V/Å. Here positive values mean the EF in [0 0 1] direction (from the Ni surface to the gas phase). While, when we evaluated the effect of co-adsorbed oxygen, we used Ni (111) surface slab model with different number of oxygen atoms. Due to space limitation, just an example of our calculations is shown in this abstract. The equilibriums in reactions (2), (3) and (4) are all leaned to products side in the EF from the gas phase to the Ni surface (negative  $\Delta E_{\rm re}$  values in the right side of Table 1), which means CO<sub>2</sub> methanation is promoted in this EF direction. This tendency is caused by the destabilization of reactants (CH<sub>3</sub> in reaction (4)) or the stabilization of products (O, CO in reactions (2), (3)) with an EF as shown in Table 1 (left side). Other results and detailed discussion will be reported at our presentation in this conference.

Table 1. Effects on the adsorption energy (left side) and the reaction energy (right side) of the electric field.

External field (V/Å)		$\Delta E_{ad}$ (eV)						External Gald (V/Å)	$\Delta E_{\rm re} (eV)$			
	Н	0	СН	со	CH <sub>3</sub>	CO <sub>2</sub>	СНО	External new (V/A)	$CHO^* + * \rightarrow CH^* + O^*$	* $CO_2^* + * \rightarrow CO^* + O^*$	$\mathrm{CH}_3{}^* + \mathrm{H}{}^* \to \mathrm{CH}_4 + 2{}^*$	
0.50	0.02	0.08	-0.10	0.13	-0.24	-0.01	-0.10	0.50	0.08	0.23	0.22	
0.25	0.00	0.03	-0.04	0.07	-0.11	0.01	-0.04	0.25	0.03	0.10	0.10	
-0.25	-0.01	-0.04 👢	0.02	-0.11	0.08	-0.05	0.00	-0.25	-0.02	-0.10	-0.07 🦊	
-0.50	-0.01	-0.08	0.04	-0.25	0.15	-0.16	-0.02	-0.50	-0.02	-0.17	-0.14	

#### References

Atami R., Ishiyama T., Kishimoto H., Katherine D.B., Yamaji K., Yamaguchi T., Fujishiro Y. Effects of Electrode Overpotential on  $CO_2$  Hydrogenation via Solid Oxide Electrolysis Cell. J Fuel Cell Tech 2016:16(2):76-80.

Sekine Y., Masayuki H., Masahiko M., Eiichi K. Low temperature steam reforming of methane over metal catalyst supported on  $Ce_xZr_{1-x}O_2$  in an electric field. Catal Today 2011:171:116-125.

Vayenas C.G., Bebelis S., Neophytides S. Non-Faradaic Electrochemical Modification of Catalytic Activity. J Phys Chem 1988:92:5083-5085.

\*Corresponding Author: t-ogura@kwansei.ac.jp

## Shock Wave and Modelling Study of the Dissociation Pathways of $(C_2F_5)_3N$

Elsa Tellbach<sup>1,\*</sup>, Carlos J. Cobos<sup>2</sup>, Lars Sölter<sup>1</sup>, and Jürgen Troe<sup>1</sup> Institute for Physical Chemistry, University Göttingen, Tammannstr. 6, 37077 Göttingen, GERMANY

<sup>2</sup> INIFTA, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, ARGENTINA

Keywords

kinetics, thermal decomposition, reaction mechanism.

The thermal decomposition of perfluorotriethylamine,  $(C_2F_5)_3N$ , was investigated in shock waves by monitoring the formation of CF<sub>2</sub>. Experiments were performed over the temperature range 1120 - 1450 K with reactant concentrations between 100 and 1000 ppm of  $(C_2F_5)_3N$  in the bath gas Ar and with [Ar] in the range  $(0.7 - 5.5) \times 10^{-5}$  mol cm<sup>-3</sup>. The experiments were accompanied by quantum-chemical calculations of the energies of various dissociation paths and by rate calculations, in particular for the dissociation of  $C_2F_5$  via  $C_2F_5 \rightarrow CF_3 + CF_2$ . The overall reaction can proceed in different ways, either by a sequence of successive C-N bond ruptures followed by fast C<sub>2</sub>F<sub>5</sub> decompositions, or by a sequence of alternating C-C and C-N bond ruptures. A cross-over between the two pathways can also take place. At temperatures below about 1300 K, yields of less than one  $CF_2$  per  $(C_2F_5)_3N$  decomposed were observed. On the other hand, at temperatures around 2000 K, when besides the parent molecule also CF<sub>3</sub> dissociates, yields of six  $CF_2$  per  $(C_2F_5)_3N$  decomposed were measured. The rate-delaying steps of the dissociation mechanism at intermediate temperatures were suggested to be the processes  $(C_2F_5)NCF_2 \rightarrow (C_2F_5)N + CF_2$  and  $(CF_2)N \rightarrow N + CF_2$ . The reduction of the CF<sub>2</sub> yields at low temperatures was tentatively attributed to a branching of the mechanism at the level of  $(C_2F_5)_2NCF_2$ , from where the cyclic final product perfluoro-N-methylpyrrolidine,  $(C_4F_8)NCF_3$ , is formed which was identified in earlier work from the literature.

#### References

Cobos, C. J. et. al., Phys. Chem. Chem. Phys, 2019. DOI: 10.1039/C9CP01142K

## THEORETICAL KINETIC STUDY OF FORMIC ACID CATALYZED KETO-ENOL TAUTOMERIZATIONS FOR C<sub>2</sub> AND C<sub>3</sub> ENOLS AT CONDITIONS RELEVANT TO ATMOSPHERIC AND COMBUSTION CHEMISTRY

E. Grajales-Ganzález<sup>1,\*</sup>, M. Monge-Palacios<sup>1</sup> and S. Mani Sarathy<sup>1</sup>

<sup>1</sup>King Abdullah University of Science and Technology (KAUST), Clean Combustion Research Center (CCRC), Physical Science and Engineering (PSE), Thuwal 23955-6900, SAUDI ARABIA.

Keywords

Keto-enol tautomerization, Combustion chemistry, Atmospheric chemistry, Tunneling, Kinetic modeling.

Enols are important species in combustion and atmospheric processes. However, their quantitative relevance has not been well established yet due to a lack of accurate chemical kinetic parameters. In this work, we compute rate constants of the formic acid assisted keto-enol tautomerization of several representative enols: (Z/E)-1-propenol and propen-2-ol, leading to propanal and acetone, respectively. In addition, the same type of tautomerization from vinyl alcohol to acetaldehyde is revisited. Forward and reverse rate constants are calculated based on high level electronic structure calculations at the CCSD(T)/aug-cc-pVYZ/M06-2X/cc-pVTZ level (Y = T/Q), including variational effects, multi-structural torsional anharmonicity and small curvature tunneling coefficients.

The adiabatic potential energy curves of the studied reactions turned out to be very narrow, enhancing a tunneling mediated mechanism which is not well described by the Eckart approach used in former studies (da Silva, 2010 and Peeters et al., 2015). The effect of the multiple conformers of the reactants, also missed in previous studies, is of some importance at high temperatures. This indicates the need to revisit previous calculations.

Kinetic modeling of the combustion of *sec-*, *n-*, and *iso-*butanol (potential alternative fuels) using our calculated rate constants proves that former kinetic models overestimate the consumption of vinyl alcohol as well as the yield of acetaldehyde. Our calculated rate constants are also used to define new analogue reactions in order to describe the fate of larger enols, aldehydes and ketones for which there are not available rate constants. They may also help to correct the underestimation of organic acids concentrations in current atmospheric models.

#### References

da Silva G. Carboxylic acid catalyzed keto-enol tautomerizations in the gas phase. Angew Chem Int Ed 2010;49:7523-7525.

Peeters J, Nguyen VS, Muller JF. Atmospheric Vinyl Alcohol to Acetaldehyde Tautomerization Revisited. J Phys Chem Lett 2015;6:4005-4011.

\*Corresponding author: edwing.grajalesgonzalez@kaust.edu.sa

## **THE ICCK 2019 CONFERENCE PROCEEDINGS**

Reaction pathways of cyclopentanone oxidation intermediates

Sarah Khanniche<sup>1</sup> and William H. Green<sup>1,\*</sup>

<sup>1</sup> Department of Chemical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue Cambridge, MA, 02139, USA

Keywords: biofuel, Ab initio calculations, kinetics, peroxy radicals

ICCK 2019, Paper format, Style template files, Word, .pdf files.

Despite the promising role of cyclopentanone as a bio-derived fuel, thermodynamic and kinetic data are lacking for low temperature oxidation regimes. This talk will present *ab initio* calculations of the subsequent reactivity that results from O<sub>2</sub>-addition to 2- and 3-oxo cyclopentyl radicals, including expected reaction classes such as intra-H migration, HO<sub>2</sub>-elimination, cyclic ether formation and  $\beta$ -scission along with their thermodynamic parameters. Some of the rates are similar to the analogous reactions of cyclopentane, but some other reactions of cyclopentanone are very different. Comparison of the reactivity of  $\alpha$ - and  $\beta$ - substituted ketone will also be discussed. These findings will be valuable for evaluating the potential of cyclopentanone as a biofuel.

## How can cells detect and respond to oxygen levels? Computer simulations studies of oxygen diffusion into prolyl hydroxylases

Carmen Domene<sup>1,2,\*</sup>

<sup>1</sup>Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AX, UK <sup>2</sup>Department of Chemistry, University of Oxford, Chemistry Research Laboratory, Mansfield Road, Oxford OX1 3PS, UK

Keywords: oxygenases, oxygen sensing, MD simulations, free energy methods, QMMM

The human body is able to sense changes in atmospheric oxygen levels and adjust its metabolic activities to suit the local environment. This is why we are able to live at a variety of altitudes ranging from below sea level to up on mountains high. How can cells detect and respond to oxygen levels?

Prolyl Hydroxylase Domain-2 (PHD2) is the most important of the human PHDs that enzymes involved in oxygen sensing. PHDs are a member of the 2OG-dependent dioxygenase family of enzymes that use dioxygen to catalyze a post-translational hydroxylation reaction in the human oxygen sensing cycle. The mechanism of catalysis involves a slow diffusive entry of dioxygen into the active site of PHD2. Work using equilibrium classical molecular dynamics simulations, coupled with biased sampling methods, non-equilibrium steered MD (SMD) and adaptive biasing force as well as Markov state models have been used to study the mechanism and kinetics of oxygen diffusion from the bulk solvent to the iron-coordinated active site. The results provide a quantitative mechanism to help understand the oxygen-sensing properties of PHD/2OG-dependent dioxygenases.

## THE PYROLYSIS CHEMISTRY OF PROPIONIC ACID AND ETHYL PROPIONATE REVEALED

Cory Rogers<sup>1</sup>, Katherine Cummins<sup>1</sup>, Jessica Porterfield<sup>2,3</sup>, John W. Daily<sup>1</sup>, G. Barney Ellison<sup>2</sup>, and Nicole J. Labbe<sup>1,\*</sup>

<sup>1</sup>Department of Mechanical Engineering, University of Colorado Boulder, 427 UCB, 1111 Engineering Drive, Boulder, CO 80309, USA

<sup>2</sup>Department of Chemistry and Biochemistry, University of Colorado Boulder, 215 UCB, Cristol Chemistry, Boulder, CO 80309, USA

<sup>3</sup>Harvard-Smithsonian Center for Astrophysics, Harvard University, 60 Garden Street, Cambridge, MA 02138, USA

Keywords

Methyl esters, Photoionization mass spectrometry, Potential Energy Surfaces, Well skipping reactions

It is well known that ethyl propionate (CH<sub>3</sub>CH<sub>2</sub>C(=O)OCH<sub>2</sub>CH<sub>3</sub>), a methyl ester sometimes used as a biodiesel surrogate, decomposes primarily via a 6-centered ring transition into propionic acid (CH<sub>3</sub>CH<sub>2</sub>C(=O)OH) and ethylene (CH<sub>2</sub>=CH<sub>2</sub>) upon heating. Thus, propionic acid is the key intermediate species for understanding the pyrolysis chemistry of ethyl propionate, though the branching ratio for the products of propionic acid pyrolysis vary among published kinetic mechanisms (Farooq et al., 2014; Dayma et al., 2012). In order to elucidate the true decomposition pathways for propionic acid, and subsequently ethyl propionate, a combination of electronic structure theory and microreactor experiments was employed. Propionic acid was heated in a microreactor under dilute conditions. The microreactor wall temperature was varied over 300-1600 K and the pressure was ~100 Torr. The products were analyzed using time of flight photoionization mass spectrometry and Fourier transform infrared spectroscopy. Concurrently, a theoretical study to characterize the pyrolysis potential energy surface and subsequent rate constants for propionic acid at the CCSD(T)/cc-pV∞Z//M06-2X/cc-pVTZ level of theory was conducted. The combination of theory with experiment revealed multiple pathways to form the main observed experimental products (methyl ketene (CH<sub>3</sub>CH=C=O), ketene  $(CH_2=C=O)$ , methyl radical  $(CH_3)$ , and ethylene  $(C_2H_4)$ ). While most products were readily explained through homolytic bond scission pathways on the propionic acid potential energy surface, it was revealed that a well-skipping pathway to methyl ketene and water via the diol well contributed to the formation of methyl ketene at the low-pressure conditions of the microreactor.

#### References

Farooq A, Davidson DF, Hanson RK, Westbrook CK. A comparative study of the chemical kinetics of methyl and ethyl propanoate. Fuel 2014;134:26-38.

Dayma G, Halter F, Foucher F, Mounaim-Rousselle C, Dagaut P. Laminar burning velocities of C4-C7 ethyl esters in a spherical combustion chamber: Experimental and detailed kinetic modeling. Energy Fuels 2012;26:6669-6677.

## Thermal decomposition of spray in plug-flow reactor at atmospheric pressure

Munko Gonchikzhapov<sup>1,\*</sup>,Tina Kasper<sup>1</sup> <sup>1</sup>University of Duisburg-Essen, 47057 Duisburg, Germany

Keywords

Spray-Syn Flame, Thermal decomposition, Nanoparticles precursors, Plug-flow reactor

The wide application of nanoparticles in industry, especially in materials science, imposes strict requirements on their geometric characteristics because the physical properties of the final material directly depend on the size. One of the main methods of nanoparticles synthesis is "Spray Flame Synthesis". A standardized Spray-Syn Burner is used, to investigate all aspects of the nanoparticle formation process. However, in the experimental study of the chemical transformation of precursors to particles in the flame it is problematic to separate contributions of the thermal decomposition and oxidation from spray formation. This work focusses on the investigation of the chemical reactions occurring during spray formation.

The Spray-Syn burner consists of four main parts: liquid channel, dispersion gas, pilot flame and co-flow. On the center there is capillary for injection of liquid. The spray is generated by dispersion gas from a co-centric dispersion channel. A methane/oxygen pilot flame stabilized on sintered matrix ignites the formed spray. A co-flow is used for stabilization of this flame.

The temperature distribution was measured by Pt/Pt-13%Rh thermocouples with junction diameters of 120 microns. The measured spatial temperature distribution of the Spray-Syn Flame shows a large region with relatively low temperatures up to 1000 °C, while the peak temperature in the flame is around 2000 °C. The reason of this low temperature region is the central dispersion gas with high velocity which prevents the formed spray from going directly to the extremely hot region.

The thermal decomposition of the spry was investigated in a heated plug flow reactor (PFR) by micro probe sampling and TOF mass-spectrometry with high resolution (m/ $\Delta$ m=4000). The micro probe was equipped an auto-cleaning system for protection from clogging. The PFR was heated from 100 °C to 800 °C with a step width of 100 °C. The composition of the sprayed solution was as follows: Ethanol/Iron pentacarbonyl (FPC), Ethanol/Titanium tetra isopropoxide (TTIP), o-xylene/FPC, o-xylene/TTIP. Mole fraction profiles of solution components were measured as function of temperature. FPC starts to decompose at the same time as ethanol at 500 °C. FPC decomposes before o-xylene (800°C) at ~500-600 °C. It means that precursors decompose in liquid phase for some cases as FPC. A solution of o-xylene with TTIP shows the same behavior, but the signal from TTIP in ethanol solution is significantly smaller than in o-xylene solution at the same concentration. The difference is most likely caused by the reaction of TTIP with water from ethanol and decomposition to TiO<sub>2</sub> and isopropanol. This fact indicates that the choice of the solvent must be made wisely.

\*Corresponding author: e-mail address

## Gas-phase rate coefficients for the reaction of the NO<sub>3</sub> radical with a series of aromatic aldehydes

Yangang REN<sup>1</sup>, Max McGillen<sup>1,2</sup>, A.R. Ravishankara<sup>1,2,3\*</sup>, Steven S. Brown<sup>4,5</sup>, Li Zhou<sup>1,6</sup>, Mahmoud Idir<sup>1</sup>, Véronique Daële<sup>1</sup>, Abdelwahid Mellouki<sup>1,\*</sup>

<sup>1</sup>CNRS-INSIS, Institut de Combustion, Aérothermique, Réactivité et Environnement 1C, Avenue de la recherche scientifique, 45071 Orléans cedex 2, France

<sup>2</sup>Le Studium Loire Valley Institute for Advanced Studies, Orléans, France.

<sup>3</sup>Departments of Chemistry and Atmospheric Science, Colorado State University, Fort Collins, CO 80253, USA

<sup>4</sup>NOAA Earth System Research Laboratory (ESRL) Chemical Sciences Division, 325 Broadway, Boulder, CO

80305, USA

<sup>5</sup>Department of Chemistry, University of Colorado Boulder, Boulder, CO 80309, USA

<sup>6</sup>Now at: National Engineering Research Center for Flue Gas Desulfurization, Department of Environmental Science and Engineering, Sichuan University, Chengdu, 610065, China

#### Keywords

Aromatic aldehyde, unsaturated VOCs, NO<sub>3</sub>, rate coefficient.

Aromatic aldehydes are a class of volatile organic compound with natural sources such as biomass burning and anthropogenic sources such as industrial activities. Their atmospheric loss processes and their consequences to the atmosphere are of interest. Yet, very few rate coefficients are available for the reactions of these species with atmospheric oxidants, especially with the NO<sub>3</sub> radical that can be ubiquitous at night.

Therefore, we have determined the rate coefficients for the reaction of NO<sub>3</sub> radical with a series of aromatic aldehydes in the gas phase using both a direct method developed recently in our laboratory (Zhou et al., 2019) and the well-established relative rate method. To ensure the accuracy of our method, we also measured the rate coefficients for NO<sub>3</sub> radical reactions with several VOCs whose rate coefficients are reasonably well-known (including isoprene, methacrolein, crotonaldehyde, and methyl vinyl ketone). Good agreement between our measured values with those in literature suggests that our methods yields accurate data. Rate coefficients of NO<sub>3</sub> with the studied aromatic aldehydes (Benzaldehyde, o-Tolualdehyde, m-Tolualdehyde, p-Tolualdehyde, 2,4-Dimethylbenzaldehyde, 2,5-Dimethylbenzaldehyde and 3,5-Dimethylbenzaldehyde ) were found to be in the range of  $2.6 \times 10^{-15}$  to  $1.6 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at atmosphere pressure (1000±5 hPa) and room temperature (298±1.5 K).

Based on our measured rate coefficients, we suggested that loss via  $NO_3$  reaction can be a minor pathway for benzaldehyde, o-tolualdehyde, m-tolualdehyde and p-tolualdehyde in the atmosphere where their reaction with OH is likely to be their primary loss process. However, for dimethyl aldehydes, their loss via  $NO_3$  reaction can be competitive with their loss via OH reaction, especially in regions with large  $NO_x$  emissions and in the dark. The results obtained will be presented and discussed.

#### Reference

Zhou, L.; Ravishankara, A. R.; Brown, S. S.; Zarzana, K. J.; Idir, M.; Daële, V.; Mellouki, A., Kinetics of the reactions of NO3 radical with alkanes. *Physical Chemistry Chemical Physics* 2019, *21* (8), 4246-4257.

#### Acknowledgement

This work has received funding from the E. U. Horizon 2020 research and innovation programme through the EUROCHAMP-2020 Infrastructure Activity under grant agreement No 730997, from the French National Research Agency (ANR), convention ANR-13-BS06-0002-01, and as part of the "Investments d'Avenir" Programme (LabEx Voltaire; ANR-11-LABX-0034), and from the PIVOTS project, co-funded by Région Centre – Val de Loire and the European Union (Europe invests in Centre-Val de Loire with the European Regional Development Fund).

# Preliminary results on syngas kinetic mechanism optimization using the new *Opt-D*<sup>\*</sup> algorithm

S M Ali \*1 and S Varunkumar<sup>2</sup>

<sup>1</sup>Department of Aerospace Engineering, Indian Institute of Technology Madras, Chennai - 600 036 <sup>2</sup>Department of Mechanical Engineering, Indian Institute of Technology Madras, Chennai - 600 036

#### Keywords Counterflow non-premixed flames, Extinction strain rate, Syngas kinetics, Optimization

Kinetic mechanisms are optimized for prediction of extinction strain rate  $(a_g)$  generally obtained from opposed jet counter-flow non-premixed flames and an equivalent 1D framework. Such mechanisms, when used to simulate 2D flames established around the boundary layer of oxidizer flow past a porous cylinder issuing fuel (Tsuji burner), over-predict  $a_g$  by up to 40% compared to experimental results (for methane). This discrepancy is shown to be related to the invalidity of plug flow boundary condition and flow field modification by flame surface assumed in 1D formulation, which in reality is not satisfied in opposed jet counter-flow experiments. A methodology has been developed to overcome these limitations of *opposed jet counter-flow configuration*, but will not be discussed here. Instead, a new optimization procedure based on extinction strain rate data obtained from Tsuji type burner (where, plug flow boundary conditions are always valid) will be applied for optimization of a syngas kinetic mechanism taken from Davis et al., (2005). The new procedure is based on the equivalence between 1D and 2D simulation results, established by comparing the flame structure obtained from 2D (by systematically varying the porous cylinder diameter, D) and 1D (by varying the nozzle separation distance, L) in mixture fraction (Z) coordinates (with methane as fuel) near extinction. The porous cylinder diameter corresponding to the point of flame structure equivalence near extinction is denoted  $D^*$  and the procedure is known as  $Opt-D^*$  algorithm. Kinetic mechanisms optimized using this algorithm is expected to have general validity for multi-dimensional laminar flames. By using syngas as fuel, preliminary results from experiments on Tsuji burner, 1D and 2D calculations will be presented. The new optimization procedure will be applied to the mechanism reported in Davis et al., (2005) using extinction strain rate as the objective function. A short mechanism will be proposed from the optimized detailed mechanism.

#### References

Davis, Scott G., et al. "An optimized kinetic model of  $H_2/CO$  combustion." Proceedings of the combustion Institute 30.1 (2005): 1283-1292.

<sup>\*</sup>Corresponding author: smughees.ali@gmail.com

## Atmospheric Oxidation Mechanism of Toluene Initiated by OH **Radical**

Xiaoqing Wu<sup>1</sup>, Can Huang<sup>1,2</sup>, Feng Zhang<sup>1\*</sup>

<sup>1</sup>National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui, 230029, P. R. China <sup>2</sup>Center for Combustion Energy and Key Laboratory for Thermal Science and Power Engineering of MOE, Tsinghua University, Beijing, 100084, P. R. China

#### Keywords

Toluene, OH radical, Oxidation mechanism, Particle-in-the-box approximation, RRKM/master equation

The toluene-OH oxidation reaction is contributed to generate urban photochemical smog in the atmosphere, which has significant impacts on air quality, human health, and climate (Ji et al., 2017). However, its detailed oxidation mechanism has not reached the same conclusion from previous theoretical and experimental results. Especially, the rate constants and branching ratio of OH addition to ortho, para, meta, and ipso positions at low temperatures remain uncertain in theory. Previous work mainly focused on the refinement of barrier heights to resolve this problem, however, ignored the large deviation caused by the low vibrational frequency anharmonicity of prereaction complex (Kovacevic and Sabljic, 2017). In the present work, oxidation of toluene is systematically studied by high-level quantum chemical method combined with RRKM/master equation calculation. The potential energy surface of both H abstraction and substitution reactions, especially the initial addition reaction of the substitution reaction, was built at the level of CCSD(T)-F12/cc-pVTZ-F12//B2PLYPD3/6-311++G(d,p) (Fig. 1). Temperature- and pressuredependent rate coefficients and branching ratio for all paths were obtained. The anharmonicity of low vibration frequency corresponding to the relative motion of OH and toluene in the complex was treated with the two-dimensional particle-in-the-box approximation for its flat potential (Fig. 2). The rate constant can be increased to reduce the deviation from the experimental value for more accurate model prediction of toluene oxidation system.



Fig.1. Potential energy surfaces for OII-toluene reaction (CCSD(T)-F12/cc-pVTZ-F12//B2PLYPD3/6-311++G(d,p))

particle-in-the-box approximation (b)

#### References

[1]Ji YM, Zhao J, Terazono H, Misawa K, Levitt NP, Li YX, Lin Y, Peng JF, Wang Y, Duan L, Pan BW, Zhang F, Feng XD, An TC, Ortiz WM, Secrest J, Zhang AL, Shibuya K, Molina MJ, Zhang RY. Reassessing the atmospheric oxidation mechanism of toluene. PNAS 2017:114:8169-8174

[2]Kovacevic G, Sabljic A. Atmospheric oxidation of halogenated aromatics: comparative analysis of reaction mechanisms and reaction kinetics. Environ. Sci. 2017:19:357-369.

\*Corresponding author: e-mail address

### Instabilities of H<sub>2</sub>-O<sub>2</sub> system and effect of several bath gases.

## P. Sabia<sup>1</sup>, M.V. Manna<sup>1,2</sup>, M. de Joannon<sup>1</sup>, R. Ragucci<sup>1</sup>

1. Istituto di Ricerche sulla Combustione - C.N.R., Napoli - Italy

3. University Federico II, Napoli, Italy

#### Introduction

The oxidation process of  $H_2$  and  $O_2$  systems have received a lot of attention because of it represents the first step for the development of complex kinetic schemes within the idea of their construction in a hierarchical structure.

Recently updated kinetic mechanisms for the  $H_2$ - $O_2$  system have been proposed by several authors. In this work, new experimental tests have been run for a lean  $H_2$ - $O_2$  mixture in several bath gas (CO<sub>2</sub>, N<sub>2</sub>,  $H_2O$  and Ar) in a Jet Stirred Flow Reactor. Instabilities have been experimentally detected, with temperature oscillations within the control volume for the system diluted in N<sub>2</sub> (fig. 1, grey area), while CO<sub>2</sub> and H<sub>2</sub>O suppress such phenomenologies. The capability to predict experimental data of updated detailed schemes is satisfactory when the diluent is N<sub>2</sub>, on the contrary for the other bath gases some discrepancies occur.

These results highlight the role of third-body reactions and the lack of a deep knowledge of the thirdbody collisional efficiencies for several bath gas.

An analysis of Rates of Reactions suggests temperature oscillations derive from a strong competition between the reaction  $H+O_2+M=HO_2+M$  and  $HO_2+H=OH+OH$ .

 $CO_2$  and  $H_2O$  may suppress instabilities because of the enhanced reaction rate of  $H+O_2+M=HO_2+M$  due to high third body collisional efficienciec overcomes the reaction rate of the competing reaction.



Figure 1. Experimental profiles of Temperature,  $H_2$ ,  $O_2$  for a lean ( $\Phi=0.5$ )  $H_2/O_2$  mixture diluted in  $N_2$  at 94%.

## WATER VAPOR DOES NOT CATALYZE THE REACTION BETWEEN METHANOL AND OH RADICALS

Coralie Schoemaecker<sup>1</sup>, Wen Chao<sup>2</sup>, Jim Jr-Min Lin<sup>2</sup>, Kaito Takahashi<sup>2</sup>, Alexandre Tomas<sup>3</sup>, Lu Yu<sup>4</sup>, Yoshizumi Kajii<sup>4</sup>, Sébastien Batut<sup>1</sup> and Christa Fittschen<sup>1,\*</sup> <sup>1</sup>CNRS-Université de Lille, PhysicoChimie des Processus de Combustion et de l'Atmosphère, Cité Scientifique, Bât. C11, 59650 Villeneuve d'Ascq, FRANCE <sup>2</sup>Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, TAIWAN <sup>3</sup>Sciences de l'Atmosphère et Génie de l'Environnement SAGE, IMT Lille Douai, 941 Rue Charles Bourseul, 59508 Douai, FRANCE <sup>4</sup>Atmospheric Chemistry, Department of Natural Sources, University Kyoto, Kyoto 606-8501, JAPAN

Keywords: Atmospheric chemistry, Radical reactions, OH radicals, reaction mechanism, Alcohols

Recent works by Jara-Toro *et al* (2017 and 2018) suggested that the rate coefficients of the reactions of OH radicals with alcohols would increase by up to 2 times from dry conditions to high humidity. This finding would have an impact on the budget of alcohols in the atmosphere and it was suggested, that it may explain differences in measured and modeled methanol concentrations. The results were based on the relative rate technique carried out in a small Teflon bag, which might suffer from wall reactions.

We have re-investigated this effect by measuring the rate constant directly using a coupling of a laser photolysis reactor to a FAGE instrument with direct fluorescence probe of OH radicals. Doing so, no catalytic effect of H<sub>2</sub>O could be found. Experiments in a Teflon bag were also carried out, but we were not able to reproduce the results of Jara-Toro *et al*. Further theoretical calculations show that even though water molecules can lower the barriers of reactions, the water-mediated reactions have negligible rates compared to the bare reactions, because the interaction of water cannot make up for the additional entropy cost (Chao *et al*, 2019).

#### References

Chao, W., Lin, J. J, Takahashi, K., Tomas, A., Yu, L., Kajii, Y., Batut, S., Schoemaecker, C., and Fittschen, C.: Hot paper: Water Vapor Does Not Catalyze the Reaction between Methanol and OH Radicals, Angew. Chem. Int. Ed., 2019, 58, 5013-5017

Jara-Toro, R. A., Hernandez, F. J., Taccone, R. A., Lane, S. I., and Pino, G. A.: Water Catalysis of the Reaction between Methanol and OH at 294 K and the Atmospheric Implications, Angew. Chem. Int. Ed., 2017, 56, 2166-2170

Jara-Toro, R. A., Hernandez, F. J., Garavagno, M. d. l. A., Taccone, R. A., and Pino, G. A.: Water catalysis of the reaction between hydroxyl radicals and linear saturated alcohols (ethanol and n-propanol) at 294 K, Phys. Chem. Chem. Phys., 2018, 20, 27885-27896

## Fast Pyrolysis Bio-oil Combustion Characteristics and Challenges for Kinetic Modeling

Alessio Frassoldati<sup>\*</sup>, Matteo Pelucchi, Abd Essamade Saufi, Alberto Cuoci, Carlo Cavallotti, Tiziano Faravelli, Eliseo Ranzi CRECK Modeling Lab, Department of Chemistry, Materials, and Chemical Engineering,

Politecnico di Milano, P.zza Leonardo da Vinci 32, 20133, Milano, Italy

#### Keywords

Fast pyrolysis bio-oil, FPBO surrogate, oxygenated aromatics, levoglucosan, kinetics, single droplet.

Fast pyrolysis of biomass produces a bio-oil (FPBO) with yields up to 75-80% wt (Bridgwater, 2012). These oils are completely different from petroleum fuels. Their unusual characteristics have to be taken into account because they have an impact on burner design, flame ignition and stability, emissions, and materials compatibility. FPBO are acidic liquids with low volatility, non-flammable, non-distillable. Bio-oils contain a tar and an aqueous fraction. The aqueous fraction contains the Low Molecular Weight (LMW) oxygenated compounds, while the tar are High Molecular Weight (HMW) lignin fragments. Thus, FPBO are complex mixtures of hundreds of compounds belonging to acids, aldehydes, ketones, alcohols, esters. anhydrosugars, furans, phenols, catecols, guaiacols, syringols, vanillins, etc. (Djokic et al., 2012). The modelling of bio-oil single droplet combustion needs a comprehensive approach (Saufi et al., 2019), which includes the description of physical phenomena and kinetic aspects. The kinetic modelling of bio-oil combustion is a very complex task for three reasons: i) the challenging characterization of FPBO; ii) the complexity of the oxidation mechanisms, especially of large oxygenated molecules (Pelucchi et al., 2019); iii) The fact that the initial evaporation and combustion of volatile LMW compounds is followed by polymerization and pyrolysis reactions of the HMW compounds in the liquid phase. Therefore, also reactions in the condensed phase, leading to a carbonaceous residue, have to be taken into account. While surrogate mixtures of reference components allow to tackle the first difficulty, the complexity of oxidation mechanisms can be handled using a lumping approach. This work summarizes the activity performed modeling in the context of the H2020 Residue2Heat (https://www.residue2heat.eu/ #654650) project, in terms of surrogate definition and single droplet evaporation and combustion with special emphasis to the kinetic aspects and the role of evaporation and characterization of the liquid phase.

#### References

**Bridgwater A.V.**, *Review of fast pyrolysis of biomass and product upgrading*, Biomass and Bioenergy, 2012:38:68-94.

**Djokic M.R., Dijkmans T., Yildiz G., Prins W., Van Geem K.M.,** *Quantitative analysis of crude and stabilized bio-oils by comprehensive two-dimensional gas-chromatography*, Journal of Chromatography A, 2012:1257:131-140.

**Saufi A.E., Frassoldati A., Faravelli T., Cuoci A.,** *DropletSMOKE++: A comprehensive multiphase CFD framework for the evaporation of multidimensional fuel droplets*, International Journal of Heat and Mass Transfer 2019 :131:836-853.
## Photosensitization in the air: bridging fundamental bulk processes with secondary organic aerosol production

Tropospheric aerosol particles have often been described and represented in models in a simplistic way where they were considered as non-volatile and chemically inert. Such assumptions have recently been challenged by frontline research, according to which volatile organic compounds (VOCs) and secondary organic aerosols (SOA) form a system that evolves in the atmosphere by chemical and dynamical processing including chemical interaction with oxidants. A current key issue concern in the physico-chemistry of atmospheric organic particulate matter is that the models based on available parameterizations from laboratory studies strongly underestimate SOA and do not adequately account for aerosol particle growth as it is observed in the atmosphere. The difference between ambient and modeled SOA concentrations clearly suggests that other significant sources of SOA have not yet been identified and characterized.

Furthermore, multiphase processes have also been shown to produce light absorbing compounds in the particle phase. The formation of such light absorbing species could induce new photochemical processes within the aerosol particles and/or at the gas/particle interface. A significant body of literature on photo-induced charge or energy transfer in organic molecules from other fields of science (biochemistry and water waste treatment) exists. Such organic molecules are aromatics, substituted carbonyls and/or nitrogen containing compounds – all ubiquitous in tropospheric aerosols. Therefore, while aquatic photochemistry has recognized several of these processes that accelerate degradation of dissolved organic matter, only little is known about such processes in/on atmospheric particles.

Therefore, this presentation will photosensitization in the troposphere as having a significant role in SOA formation and ageing. Such photosensitization may introduce new chemical pathways so far unconsidered impacting both the chemical composition of the atmosphere and can thus contribute to close the current SOA underestimation.

## Experimental and kinetic study of 1,2,4-trimethylcyclohexane pyrolysis

Yue-Xi Liu<sup>1,2</sup>, Dong-Xu Tian<sup>1,2</sup>, Chuang-Chuang Cao<sup>3</sup>, Zhong-Kai Liu<sup>3</sup>, Yi-Tong Zhai<sup>3</sup>, Yan Zhang<sup>3</sup>, Jiu-Zhong Yang<sup>3</sup>, and Zhen-Yu Tian<sup>1,2,\*</sup>

<sup>1</sup>Institute of Engineering Thermophysics, Chinese Academy of Sciences, 11 Beisihuanxi Rd., Beijing 100190, CHINA

<sup>2</sup>University of Chinese Academy of Sciences, 19A Yuquan Rd., Beijing 100049, CHINA

<sup>3</sup>National Synchrotron Radiation Laboratory, University of Science and Technology of China, 42 Hezuohua South Rd., Hefei 230029, CHINA

#### Keywords:

Trimethylcyclohexane, Pyrolysis, Kinetic model, SVUV-PIMS, Pressure effect.

In the past decades, the combustion studies of aviation fuels, as the energy source of aircrafts, have captured more and more attention with respect to high efficiency and low pollutant emissions. More remarkable, cycloalkanes are considered to be a major component of the aviation fuels. Alkyl cyclohexanes have been considered as the important components of surrogate model fuels in these years.

This work reports the pyrolysis studies of 1,2,4-trimethylcyclohexane (T124MCH) at 30 and 760 Torr using online synchrontron radiation photoionization and molecular beam mass spectrometry (SVUV-PIMS) techniques. The intermediates and major products were identified, and the mole fraction of these species were calculated. T124MCH pyrolysis starts at 1025 K and does not finish at 1200 K under low pressure (30 Torr). The process of pyrolysis under 760 Torr is nearly 150 K lower than the low pressure one. These temperatures are much higher than other hydrocarbons, especially aromatics. Ethene and propene are the major intermediates in pyrolysis, while benzene, toluene, and xylenes are detected as aromatic intermediates. The mechanism presented by Liu et al.<sup>[1]</sup> recently could reasonably predict the experimental result of T124MCH, but need further improvements on intermediates predictions. These results can be used to validate and extend the mechanism of T124MCH under pyrolysis conditions, which could provide a useful kinetic understanding of the chemistry of alkyl cyclohexanes and surrogate fuels.



Figure 1 Experimental and modeling results of 1,2,4-trimethylcyclohexane pyrolysis under 760 and 30 Torr

#### References

Liu YX, Yu D, Tian DX, Tian ZY. An experimental and modeling study of oxidation of 1,2,4-trimethylcyclohexane with JSR. Proc Combust Inst 2019;37(1):437-444.

## ANTHRAQUINONE-2-SULFONATE AS A MODEL FOR PHOTOINDUCED REACTIONS IN TROPOSPHERIC AQUEOUS AEROSOL

T. Schaefer<sup>1,\*</sup>, J. D. Raff<sup>2</sup>, H. Herrmann<sup>1</sup>

 <sup>1</sup>Atmospheric Chemistry Department (ACD), Leibniz Institute for Tropospheric Research (TROPOS), Permoserstrasse 15, 04318 Leipzig, GERMANY
 <sup>2</sup>O'Neill School of Public & Environmental Affairs and Department of Chemistry, Indiana University, Bloomington IN 47405, USA

Keywords

Atmospheric chemistry, Aqueous phase, Photosensitizer, Anthraquinone-2-sulfonate.

The uptake of semi-volatile organic compounds into preexisting particles is the main pathway of the secondary organic aerosol (SOA) formation in traditional models. However, studies by Monge et al. (2012), Aregahegn et al. (2013) and Rossignol et al. (2014) give hints that the chemical transformation processes occurring during aerosol aging are related to photosensitization reactions within the particles. Unfortunately, this chemistry remains highly uncertain because of an incomplete understanding of radical reactions and the mechanisms driving redox chemistry in aerosol particles. Within the present study, anthraquinone-2-sulfonate (AQS) is used as a model photosensitizer to understand the photochemical pathways in SOA formation using a laser flash photolysis-laser long path absorption setup. The time-resolved absorbance spectra ( $\lambda = 300-700$  nm) of the excited states and the reaction rate constants with molecular oxygen [ $k_{298 \text{ K}} = (5.1 \pm 1.1) \times 10^8 \text{ L} \text{ mol}^{-1} \text{ s}^{-1}$ ] and other aerosol constituents, such as iron(III) sulfate, will be presented. Finally, product analysis of the photo-induced oxidation reactions involving AQS were carried out using several analytical techniques (e.g., GC-MS).

#### References

Aregahegn KZ, Nozière B, George C. Organic aerosol formation photo-enhanced by the formation of secondary photosensitizers in aerosols. Faraday Discuss 2013; 165:123–134.

George C, Ammann M, D'Anna B, Donaldson DJ, Nizkorodov SA, Heterogeneous Photochemistry in the Atmosphere. Chem Rev 2015; 115:4218–4258.

Monge ME, Rosenørn T, Favez O, Müller M, Adler G, Riziq AA, Rudich Y, Herrmann H, George C, D'Anna B. Alternative pathway for atmospheric particles growth. Proc Nat Acad Sci USA 2012; 109:6840–6844.

## A comprehensive experimental and kinetic modeling study of *o*-xylene combustion

Wenhao Yuan<sup>1</sup>, Long Zhao<sup>2</sup>, Wei Li<sup>1</sup>, Yuyang Li<sup>1,\*</sup>, Philippe Dagaut<sup>3,\*</sup>, Fei Qi<sup>1</sup> and Jiuzhong Yang<sup>2</sup>

<sup>1</sup>School of Mechanical Engineering, Shanghai Jiao Tong University, Shanghai 200240, P.R. China <sup>2</sup>National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, P.R. China

<sup>3</sup>CNRS-INSIS, Institut de Combustion, Aérothermique, Réactivité et Environnement, 1C, Avenue de la recherche scientifique, 45071 Orléans cedex 2, FRANCE

#### Keywords

o-xylene, flow reactor pyrolysis, jet stirred reactor oxidation, kinetic model, PAHs formation.

o-Xylene is an important component in gasoline and jet fuel. In this work a comprehensive experimental and kinetic modeling study was performed to investigate the combustion of o-xylene. Flow reactor pyrolysis of o-xylene at 0.04, 0.2 and 1 atm was investigated using synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS). Jet stirred reactor (JSR) oxidation of o-xylene was investigated at 10 atm and equivalence ratios of 0.5, 1.0 and 2.0 using gas chromatography. A detailed kinetic model of o-xylene combustion with a detailed sub-mechanism of o-xylyl decomposition and oxidation was developed by extending our previous kinetic model of aromatics combustion (Yuan et al., 2017). Model analyses such as rate of production analysis and sensitivity analysis were also performed to reveal the key pathways in the consumption of fuel and formation of polycyclic aromatic hydrocarbons (PAHs). The analysis results demonstrate that under the pyrolysis conditions, the consumption of xylenes mainly proceed unimolecular C-H bond dissociation reactions and radical attack reactions. o-Xylyl radicals decompose through H loss to form closed-shell o-xylylene, which quickly isomerizes to benzocyclobutene. o-Xylylene can also generate styrene with multi-step rearrangement reactions. Low temperature reactions were found to play important roles in the oxidation of o-xylene. Under high pressure and low temperature conditions, the addition of O2 to o-xylyl mainly generates o-xylylperoxy radical, which can undergo secondary chainbranching reactions via the intramolecular H transfer reaction to form QOOH type o-(hydroperoxy)methylbenzyl radical, which can proceed further low temperature chain reactions. Under higher temperatures, the oxidation of o-xylyl mainly proceeds through reactions with O, OH and HO<sub>2</sub>, which produce methylbenzoxyl radicals as major products. Further decomposition of methylbenzoxyl radicals mainly produces methylbenzaldehyde + H. In addition, the formation pathways of PAHs are strongly related to fuel-specific reactions, especially for the formation of bicyclic PAHs such as indene and naphthalene. o-Xylylene, o-xylyl and styrene were observed as the major precursors of PAHs in o-xylene combustion. Furthermore, the present model was also validated against previous experimental data of o-xylene combustion under a wide range of conditions, including both speciation data and global combustion parameters.

#### References

Yuan WH, Li YY, Dagaut P, Wang YZ, Wang ZD, Qi F, A comprehensive experimental and kinetic modeling study of *n*-propylbenzene combustion, Combust. Flame 2017;186:178-192.

\*Corresponding author: yuygli@sjtu.edu.cn (Yuyang Li), dagaut@cnrs-orleans.fr (Philippe Dagaut)

## DEVELOPMENT AND VALIDATION OF A TEFLON THERMAL REGULATED ATMOSPHERIC SIMULATION CHAMBER (THALAMOS). A VERSATILE TOOL FOR THE STUDY OF ATMOSPHERIC RELEVANT PROCESSES.

Noureddin Osseiran,<sup>1</sup> Manolis N. Romanias,<sup>1\*</sup> Vincent Gaudion,<sup>1</sup> Maria Angelaki,<sup>2</sup> Vassileios C. Papadimitriou,<sup>2</sup> Alexandre Tomas,<sup>1</sup> Frederic Thevenet,<sup>1</sup> Patrice Coddeville.<sup>1</sup>
1 : IMT Lille Douai, Univ. Lille, SAGE, F-59000 Lille, France
2 : Laboratory of photochemistry and chemical kinetics (LAPKIN), University of Crete, 71003 Heraklion, Crete, Greece

Keywords: Thermostated simulation chamber; gas phase kinetics; VOC degradation;

Atmospheric simulation chambers (or smog chambers), are unique tools for investigating atmospheric processes in the gas and heterogeneous phases. They can provide a controlled yet realistic environment that simulates atmospheric conditions. In the framework of this study, a medium sized Teflon atmospheric simulation chamber of 600 L, named THALAMOS (THermAL regulated AtMOSpheric simulation chamber) has been developed and validated. THALAMOS can be operated over the temperature range of 233 to 373 K under both static and flow conditions. It is equipped with state of the art instrumentation (Selective Ion Flow Tube Mass Spectrometry, Long path FTIR, GC-MS, various types of analyzers) for the inline monitoring of the reactants and products. THALAMOS was validated by measuring the rate coefficients of two well documented reactions, i.e. the reaction of ethanol with OH radicals and the reaction of dichloromethane with Cl atoms in a wide temperature range. The obtained results are in excellent agreement with literature recommended values. Furthermore, the oxidation of toluene by Cl atoms was studied in the temperature range of 253 to 333 K. The rate coefficient was found to be independent on temperature, and was  $(5.85\pm0.12)\times10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Besides the kinetics, a detailed product analysis was carried out. Benzaldehyde and benzyl alcohol have been identified and quantified as the major degradation product with yields of 80±5 % and 11±4 %, respectively. To the best of our knowledge, THALAMOS is a unique facility on national level that is operated in such a wide temperature range and it is a unique tool for the study of outdoor and indoor physicochemical processes with a large range of applications.

### High-Temperature Fast-Flow Reactor for the study of Radical-Radical Reactions

Yoon Lee, Fabien Goulay Department of Chemistry, West Virginia University, Morgantown, WV 26506 – USA

#### Keywords

Radical Chemistry, High temperature flow reaction, Laser Induced Fluorescence, Gas Phase Kinetics

A novel pulsed fast-flow reactor was designed to allow for the measurement of free radical reaction rate coefficients at high-temperature using laser induced fluorescence (Figure 1). The 10-Hz pulsed fast-flow reactor delivers a uniform subsonic flow of gas at temperatures up to 800K that allows for wall-free kinetic investigations. The gas is heated and then isentropically expanded through a Laval nozzle to supersonic speeds. A vertical shockwave is formed at the exit of the nozzle by controlling the post-nozzle pressure in order to recover the reservoir temperature. The result is a laminar flow with homogeneous temperature, pressure, and number density for over 1 meter, corresponding to a hydrodynamic time of up to 1 ms. Gas pulsing is made possible by a rotating metal disk prior to the nozzle throat with an opening for the gas to travel. The design of this flow reactor allows for a reduced cost of gas volume and heating power and eliminates the need to heat near sensitive optical equipment.

Temperature measurements were conducted by measuring the rovibrational spectra of the CN radical and fitting the line intensities to a Maxwell-Boltzmann distribution. Velocity profiles were also taken at different temperatures via pitot tube to study the conditions inside of the flow. The velocity measurements within the nozzle corresponds well with the predicted velocity of the flow after the shockwave.

The fast–flow reactor will be used to measure the rate coefficients of selected radical–radical reactions at high temperatures. The radicals of interest which include the propargyl, allyl, and benzyl radical are resonantly stabilized radicals. These molecules are stable and relatively unreactive with molecular oxygen (Miller et al. 2005) and play a significant chemical role in high-temperature combustion environments (Sinha et al. 2016). The reactions of these radicals with the OH radical will be measured by LIF.



Figure 1: High-Temperature Fast Flow Reactor

Miller, J. A. et al. Proc. Comb. Inst., 30, 43 (2005); Sinha, S. et al. Phys. Chem. Chem. Phys., 18, 8120 (2016);

Yolee1@mix.wvu.edu

## Atmospheric Reactivity of Biogenic Volatile Organic Compounds under the Canopy of a Maritime Pine Forest during the LANDEX Field Campaign

Kenneth Mermet<sup>1,2,3</sup>, Stéphane. Sauvage<sup>1</sup>, Sébastien Dusanter<sup>1</sup>, Thérèse Salameh<sup>1</sup>, Thierry Léonardis<sup>1</sup>, Nadine Locoge<sup>1</sup>, Pierre-M. Flaud<sup>2,3</sup>, Émilie Perraudin<sup>2,3</sup>, Éric Villenave<sup>2,3</sup>

<sup>1</sup> IMT Lille Douai, Univ. Lille, SAGE - Département Sciences de l'Atmosphère et Génie de l'Environnement, 59000 Lille, France

<sup>2</sup> Univ. Bordeaux, EPOC, UMR 5805, F-33405 Talence Cedex, France

<sup>3</sup> CNRS, EPOC, UMR 5805, F-33405 Talence Cedex, France

Keywords: Biogenic volatile organic compounds (BVOCs), BVOC photo-oxidation, forested environment, Ozone, OH radical, nitrate radical.

Emissions of volatile organic compounds (VOCs) impact both the atmospheric oxidizing capacity and the earth's radiative balance through the formation of ozone and secondary organic aerosols (SOA). On a global scale, forests are the largest emitters of VOCs such as isoprene, monoterpenes and sesquiterpenes; once emitted in the atmosphere, they are rapidly oxidized into oxygenated species. Depending on their volatility and chemical reactivity, these oxidation products may be themselves further oxidized, remaining in the gas phase and/or being transferred to the particulate phase to formed SOA.

Trace gas and aerosol measurements were performed during summer 2017 as part of the LANDEX (the LANDes EXperiment) campaign in one of the largest European pine forests (> 95% *Pinus pinaster*) located southwestern France. A new chromatographic method was deployed to perform a speciation of 20 BVOCs, including isoprene,  $\alpha$ - and  $\beta$ -pinene, carenes, terpinene, linalool, camphene, etc. This dataset was used to assess the importance of BVOCs for the local photochemistry through an analysis of their reactivity with the main atmospheric oxidants, including the hydroxyl radical (OH), ozone (O<sub>3</sub>) and the nitrate radical (NO<sub>3</sub>).

Considering the reactivity of BVOCs with oxidants below the canopy, it is shown that isoprene and linalool account for 30-65% of the OH loss rate during daytime whereas monoterpenes are the main contributors during nighttime (70-95%). Sesquiterpenes and monoterpenes drive the ozone loss rate with maxima at night, 20-60% of the chemical O<sub>3</sub> loss being due to  $\beta$ -caryophyllene. The nitrate loss rate is also driven by monoterpenes, which accounted for 70-90% of the total nitrate reactivity. Considering the contribution of each oxidant to the total consumption of specific BVOCs, it is shown for example that  $\alpha$ -pinene was principally consumed by OH during daytime (40-55%) and by ozone at night (60-85%). Finally, the total amounts of 6 BVOCs (isoprene,  $\alpha$ -pinene,  $\beta$ -pinene, myrcene, limonene,  $\Delta^3$ -carene) oxidized above and below the forest canopy were contrasted to assess the importance of chemical processes occurring below the canopy. These results will be discussed to highlight important trace gases, oxidants and reactive processes operating below the canopy of a maritime pine forest.

# Structure of a counterflow flame at different operating conditions

Saulo A. Gómez S. \*1, Victor Zhukov<sup>2</sup>, Claudia R. de Andrade<sup>1</sup> and Amilcar P. Pimenta<sup>1</sup>

<sup>1</sup>Instituto Tecnológico de Aeronáutica (ITA), São José dos Campos, BRASIL <sup>2</sup>Institue of Space Propulsion, German Aerospace Center (DLR), Lampoldshausen, GERMANY

## Keywords: chemical kinetics, counterflow flame, flamelet, GRI-mech, methane.

Simulation of turbulent non-premixed combustion requires a complete description of the laminar counterflow diffusion flame where detailed chemistry is included through the solution of the Arrhenius expressions. The most used mechanism to study the burning of hydrocarbons is GRI-mech which provides the coefficients of the Arrhenius equations for 325 elementary reactions. However, application of this mechanism is not suitable in flames burning at pressures higher than 10 atm. Recently, Zhukov and others proposed a reduced mechanism, named as ReduceSens, in order to improve the accuracy of numerical simulations of rocket engines feed with methane and oxygen. The aim of this work is to obtain the structure of the counterflow flame generated for the combustion of methane at two pressure levels: 1 atm and 20 atm, with GRI-mech and ReduceSens respectively, which are the appropriate mechanisms in each case. In addition, effect of the content of oxygen in the oxidant is also studied in a range that goes from the normal air composition (21%  $O_2$  and 79%  $N_2$ ) until 100% oxygen. Distance between nozzles is fixed at 1.5 cm as well as the inlet velocities, 30 cm/s for both reactants. Simulation provides profiles of temperature, Fig. 1,  $H_2O$  and CO as function of the distance to the fuel-nozzle and the mixture fraction. Results show that the two parameters affect maximum values and its location. Comparison with calculation under chemical equilibrium is also discussed.



Figure 1: Temperature distribution

\*Corresponding author: sagomezs@unal.edu.co

# FIRST-PRINCIPLES KINETIC MONTE CARLO STUDY OF HYDRODEOXYGENATION AT THE RU/TIO<sub>2</sub> INTERFACE

Xiao Li<sup>1</sup> and Lars C. Grabow<sup>1,\*</sup> <sup>1</sup>Department of Chemical and Biomolecular Engineering, University of Houston, Houston, TX 77004-4004, USA

Keywords

Hydrodeoxygenation, kinetic Monte Carlo, DFT, metal-support interface.

Catalytic upgrade of bio-oil to fuels and chemicals requires the selective catalytic reduction of the various oxygenated compounds amounting to 10–40 wt% total oxygen content. For fundamental kinetic studies of this process, the hydrodeoxygenation (HDO) of phenolic compounds is a popular prototype reaction. We previously reported a positive linear relation between the toluene formation rate from *m*-cresol and the Ru perimeter length for Ru/TiO<sub>2</sub> catalyst, supporting the placement of active sites at the interface (Omotoso et al., 2017). We also reported that water partial pressure plays a significant role in increasing the hydrogenefficient, direct deoxygenation rate, which we attribute to a proton-assisted HDO mechanism (Nelson et al., 2015). While interfacial reactions and vacancies on the oxide support are frequently invoked as active sites, knowledge of the mechanism of their formation and a detailed description of reaction events across the metal-support interface are still lacking.

We have combined density functional theory (DFT) and kinetic Monte Carlo (kMC) simulations to investigate the reduction and hydroxylation properties of rutile  $TiO_2(110)$  in the presence and absence of Ru nanoparticles, as well as *m*-cresol HDO reactions, with particular focus on the Ru/TiO<sub>2</sub> interface. Our results allow us to attribute the enhanced rate of support reduction and HDO activity to H spillover and a facile, heterolytic H<sub>2</sub> cleavage pathway across the Ru/TiO<sub>2</sub> interface. Under HDO reaction conditions a coverage transition occurs at around 550 K and explains the existence of two kinetic regimes at low and high temperature. By varying the water partial pressure at constant temperature our model also predicts the experimentally observed positive reaction order for water.

To our knowledge, there exists no comparable model capable of discriminating between metal, oxide and interfacial activity, and assigning a dominant catalytic role to each component. The ability to generate such detailed fundamental insight can be leveraged for the future design of multifunctional catalysts with unprecedented selectivity advantages.

#### References

Omotoso TO, Baek B, Grabow LC, Crossley SP. Experimental and First-Principles Evidence for Interfacial Activity of  $Ru/TiO_2$  for the Direct Conversion of *m*-Cresol to Toluene. ChemCatChem 2017:9:2642-2651.

Nelson RC, Baek B, Ruiz P, Goundie B, Brooks A, Wheeler MC, Frederick BG, GrabowLC, Austin, RN. Experimental and Theoretical Insights into the Hydrogen-Efficient Direct Hydrodeoxygenation Mechanism of Phenol over Ru/TiO<sub>2</sub>. ACS Catal. 2015:5:6509–6523.



### **ATMOSPHERIC DEGRADATION OF 3-ETHOXY-1-PROPANOL**

Cabañas B.<sup>1,2</sup>, <u>Aranda I.<sup>1,2\*</sup></u>, Martín P.<sup>1,2</sup> and Salgado S.<sup>1,2</sup>.

 <sup>1</sup>University of Castilla La Mancha, Departament of Physical Chemistry, Facultad de Ciencias y Tecnologías Químicas, Avda. Camilo José Cela s/n, 13071 Ciudad Real, SPAIN
 <sup>2</sup>(ICCA) Instituto de Combustión y Contaminación Atmosférica. Universidad de Castilla La Mancha, Ciudad Real, Camino de Moledores s/n, 13005 Ciudad Real, SPAIN

Keywords

Glycol ether, rate coefficient, mechanism, products, atmospheric implications.

Some glycol ethers are used in blends with diesel fuel polished obtaining a decrease in CO, hydrocarbons or particulate matter emissions (F. Gómez-Cuenca et al, 2011). In this work, rate coefficients for the reactions of OH, NO<sub>3</sub> radicals, and Cl atoms, with 3-ethoxy-1-propanol (3E1P) have been determined using a relative rate technique with FTIR (Fourier Transform Infrared Spectroscopy) as detection system at T=  $(298\pm2)$  K and atmospheric pressure. Rate coefficients (*k* in units of cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup>) obtained were:  $(3.4\pm0.2)\times10^{-10}$ ,  $(3.5\pm0.1)\times10^{-11}$  and  $(1.6\pm0.1)\times10^{-14}$  for Cl, OH· and NO<sub>3</sub>· reactions respectively. Experiments were developed using at least three reference compounds (example: figure 1).

Qualitative product analysis was developed using FTIR and GC-MS (Gas Chromatography/Mass Spectrometry) techniques. The main products were carbonyl compounds such as ethyl formate and formaldehyde. These results support a mechanism involving initial oxidant attack at the –CH<sub>2</sub>- groups. The tropospheric lifetimes calculated suggest that the dominant loss process for 3E1P is clearly the daytime reaction with the OH radical.



Figure 1. Relative rate plots for the reaction of 3-ethoxy-1-propanol (3E1P) with Cl atoms using two reference compounds.

#### References

Gómez-Cuenca F, Gómez-Marín M, Folgueras-Díaz MB. Effects of ethylene glycol ether on diesel fuel properties and emissions in a diesel engine. Energy Convers. and Manag. 2011;52:3027-3033.

\*Corresponding author: inmaculada.aranda@uclm.es

# Organo-phosphorous fire suppressants and their reactions with H atoms

Pascal Diévart<sup>\*1</sup> and Laurent Catoire<sup>1</sup>

<sup>1</sup>Unité Chimie et Procédés (UCP), ENSTA-ParisTech, 91762 Palaiseau cedex, FRANCE

Keywords

fire suppressants ; organo-phosphorous compounds ; H atom ; rate constant ; quantum chemistry

The Montreal protocol banned Halon-1301, thus calling for substitutes that are as efficient as combustion inhibitors. OrganoPhosphorous compounds (OPCs) are such candidates, as suggested by the early works of Twarowski (1993). Experimental studies have been since conducted, mostly investigating the effect of the addition of dimethyl methyl phosphonate (DMMP) and trimethyl phosphate (TMP) to hydrogen/air, methane/air, and propane/air flames, either in premixed (Korobeinichev et al., 1999; Li et al., 2019) or in diffusion configuration (Bouvet et al., 2016; Li et al., 2019). The fire suppressant effect of the phosphorous additives was supported by the experimental observations: slower laminar flame velocities or a decrease in the  $CO_2$  extinguishing concentration. Recently, Mathieu et al. (2019) investigated the effect of DMMP on the ignition properties of different fuel mixtures.

Kinetic models have also been proposed, focusing mainly on the two surrogates DMMP and TMP (Babushok et al., 2016; Glaude et al., 2002; Jayaweera et al., 2005; Koroibenichev et al., 2000). The phosphorous subset in these models were developped on the earlier suggestions of Twarowski et al. (1993), augmented by specific reactions of the OPCs investigated, and finally tested against flame data, especially laminar flame speeds. Meanwhile, Sullivan et al. (2004) and Khalfa et al. (2015) performed quantum chemical calculations with composite methods (CBS-Q and CBS-QB3, respectively) to refine the thermochemistry of organophosphorous compounds and update Benson's group contribution tables.

Although the kinetic models currently available capture to some extent the experimental observations, further improvements require a deeper understanding of the chemistry of the P-bearing species. The current study presents rate constants for the H abstraction reactions by the H atom from a set of phosphorous compounds. The choice of H atom as the scavenger was motivated by its preponderance in flames, and by the results of Mathieu et al. (2019) who identified the DMMP + H reaction as one of the most sensitive reaction in governing DMMP ignition. Potential Energy Surfaces of the investigated reactions were obtained with different level of theory: CBS-QB3, G3X-K (da Silva et al., 2013), CCSD(T)/cc-pV $\propto$ Z //M06-2X/aug-cc-pVDZ, and CCSD(T)/cc-pV $\propto$ Z //B2PLYP/aug-cc-pVDZ level of theory. Geometry, frequency, composite energy, and hindered rotors barrier calculations were performed with the software GAUSSIAN 09 (Frisch et al., 2013) while CCSD(T) and DLPNO-CCSD(T) energy calculations were done with Orca 4.1.0 (Neese, 2017; Saitow et al., 2017). Rate constants were finally calculated with the Multiwell Program Suite (Barker et al., 2017) with

<sup>\*</sup>Corresponding author: pascal.dievart@ensta-paristech.fr

## Calculation of the Absolute Photoionization Cross-Sections for C1-C4 Criegee Intermediates and Vinyl Hydroperoxides

Can Huang<sup>1,2</sup>, Bin Yang<sup>1</sup> and Feng Zhang<sup>2,\*</sup>

<sup>1</sup> Center for Combustion Energy and Key Laboratory for Thermal Science and Power Engineering of MOE, Tsinghua University, Beijing, 100084, P. R. China

<sup>2</sup> National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui, 230029, P. R. China

Keywords

Cross section, Criegee intermediate, Vacuum ultraviolet photoionization, vinyl hydroperoxide, Carbonyl oxide

Criegee Intermediates (CIs) and their isomer Vinyl Hydroperoxides (VHPs) are crucial intermediates in the ozonolysis of alkenes. To better understand the underlying chemistry of CIs and VHPs, progress has been made to detect and identify them by photoionization mass spectrometric experiments. Further reliable quantitative information about these elusive intermediates requires their photoionization cross sections. The present work systematically investigated the near-threshold absolute photoionization cross-sections for ten C1-C4 CIs and VHPs, i.e. Formaldehyde oxide (CH<sub>2</sub>OO); Acetaldehyde oxide (syn-/anti-CH<sub>3</sub>CHOO) and Vinyl hydroperoxide (CH<sub>2</sub>CHOOH); Acetone oxide ((CH<sub>3</sub>)<sub>2</sub>COO) and 2-hydroperoxypropene (CH<sub>2</sub>=C(CH<sub>3</sub>)OOH); syn-CH<sub>3</sub>-anti-(trans-CH=CH<sub>2</sub>)–COO, syn-CH<sub>3</sub>-anti-(cis-CH=CH<sub>2</sub>)–COO. The adiabatic ionization energies (AIE) were calculated at the DLPNO-CCSD(T)/CBS level. The calculated AIE for C1-C4 CIs and VHPs vary from 8.75-10.0 eV with the AIE decreasing as the substitutions increase. Pure electronic photoionization cross sections are calculated by the frozen-core Hartree-Fock (FCHF) approximation. The final determined absolute cross sections are around 4.5-6 Mb for the first and second ionization of CIs and 15-25 Mb for VHPs. It is found that the addition of a methyl group or an unsaturated vinyl substitution for the Criegee intermediates does not substantially change the absolute value of their cross section.



Figure 1 Structures of the carbonyl oxide substitutions and the corresponding vinyl hydroperoxides examined in this work.

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

## Quantum Chemical Study of Decomposition and Condensation Reactions of Urea

Dennis Gratzfeld and Matthias Olzmann<sup>\*</sup> Institut für Physikalische Chemie, Karlsruher Institut für Technologie (KIT), Kaiserstr. 12, 76131 Karlsruhe, Germany

Keywords

Urea, s-Triazines, Coupled Cluster Theory, Standard Enthalpies of Formation, Potential Energy Surfaces

Urea decomposition and condensation reactions are of crucial importance in several biological systems and technical processes. In addition to being a widely used nitrogen fertilizer, urea is applied in the urea-based selective catalytic reduction (urea-SCR) to reduce the NO<sub>x</sub> emissions of mobile lean-burn combustion devices. Here, urea-water solution is directly injected into the exhaust stream, producing in situ the reducing agent ammonia by catalytic thermolysis and hydrolysis. The chemical mechanisms governing these processes are, largely, still not clear. Particularly, the formation of byproducts such as biuret and s-triazines is not fully understood, which presents a challenge for technical applications, as these byproducts can develop into solid deposits impairing the performance of the exhaust after treatment.

We performed high-level quantum chemical calculations to gain insight into this complex reaction system. Starting with the calculation of the most fundamental molecular data, the standard enthalpies of formation, we went on to characterize reaction pathways and stationary points on relevant potential energy surfaces of homogeneous gas-phase reactions with explicitly correlated coupled cluster and density functional theory calculations. First results showed that a purely homogeneous mechanism is not able to explain the extent of byproduct formation observed in experiments, leading us to a more detailed study of the influence of water on the kinetics. The catalytic effect of a growing number of water molecules is investigated and mechanistic consequences are discussed.

## KINETICS OF OH RADICALS WITH HNO<sub>3</sub> BETWEEN 21.7 K AND 177.5 K IN THE GAS PHASE

Daniel González<sup>1</sup>, Sergio Blázquez<sup>1</sup>, A. R. Ravishankara<sup>2</sup> and Elena Jiménez<sup>1,\*</sup> <sup>1</sup> Departamento de Química Física, Facultad de Ciencias y Tecnologías Químicas, Universidad de Castilla-La Mancha, Avda. Camilo José Cela 1B, 13071 Ciudad Real, SPAIN <sup>2</sup>Departments of Chemistry and Atmospheric Science, College of Natural Sciences, Colorado State University, 1872 Campus Delivery. Fort Collins, CO, USA 80523-1872

#### Keywords

CRESU technique, ultra-low temperatures, non-Arrhenius behavior.

Nitric acid (HNO<sub>3</sub>) is produced by the reaction of hydroxyl (OH·) with NO<sub>2</sub> (and hydrolysis of N<sub>2</sub>O<sub>5</sub>) in Earth's atmosphere. HNO<sub>3</sub> formation in the troposphere terminates of NOx (NO<sub>2</sub> + NO). However, in the upper troposphere and stratosphere (UTLS) (where the mean temperature is ~210-250 K), HNO<sub>3</sub> can be converted back to NO<sub>x</sub> by reaction with OH radicals:

 $OH \cdot + HNO_3 \rightarrow H_2O + NO_3 \cdot k(T)$  (1) Photolysis of NO<sub>3</sub> · increases the NO<sub>x</sub> and, therefore, reaction (1) plays an important role in controlling the O<sub>3</sub> budget via the NO<sub>x</sub> catalysis of ozone formation and catalysis of O<sub>3</sub> removal.

The gas-phase kinetics of reaction (1) has widely been investigated at temperatures higher than 200 K, where the negative temperature dependence of the rate coefficient k(T) has been well established. It has been shown that this reaction occurs through the formation of an OH-HNO<sub>3</sub> complex in the entrance channel for the reaction leading to unusual temperature and pressure dependencies.

The interest of the OH+ HNO<sub>3</sub> reaction at T<200 K is also linked to chemistry in planets with Earth-like atmospheres with a high content of NO<sub>x</sub>, where OH radicals have recently been detected, for example in the nightside of Venus' upper mesosphere and more recently in Mars.

The goal of this work is to determine the temperature dependence of k(T) for reaction (1) at very low temperatures where the OH-HNO<sub>3</sub> adduct formation can be highly enhances. We studied this reaction between 21.7 K and 177.5 K using the uniform supersonic expansion technique for cooling the gas coupled to the pulsed laser photolysis/laser induced fluorescence kinetic technique (Jiménez et al., 2015). Within this temperature range, k(T) was observed to be greatly enhanced relative to that at room temperature. Such behavior has been seen in many other OH-reactions. The potential pressure dependence of k(T) has been measured at several temperatures.

#### References

Jiménez E, Ballesteros B, Canosa A, Townsend TM, Maigler FJ, Napal V, Rowe BR, Albaladejo J, Rev Sci Instrum 2015; 86: 45108, 1–17.

## Theoretical study on the Hydrogen abstraction reactions from hydrazine derivatives by H atom

Nozomu Kanno\* and Tomohiro Kito

Department of Vehicle and Mechanical Engineering, Faculty of Science and Technology, Meijo University, 1-501 Shiogamaguchi, Tempaku-ku, Nagoya 468-8502, JAPAN

Keywords

Hydrazine derivatives, H atom abstraction, Substitution effect.

Hydrazine and its methyl derivatives are widely used fuels for space craft rocket thrusters. In the present study, hydrogen abstraction reactions from  $N_2H_4$ ,  $CH_3NHNH_2$ , and  $(CH_3)_2NNH_2$  by H atom have been theoretically The reactants, the products, and the minimum energy paths were calculated using the investigated. CBS-QB3//DSD-BLYP-D3(BJ)/Def2-TZVP level of theory. For the  $N_2H_4$  + H reaction, the calculated energies agreed well with those reported by Li et al. (2003) calculated at the PMP4/6-311+G(3df,p2d)//UMP2/ 6-31+G(d,p) level of theory. Both the products and the transition states energies were decreased with increasing the number of methyl group substitutions. For the H abstraction from amino group, the substitution effect per each methyl group for  $\alpha$  site, i.e. CH<sub>3</sub>NNH<sub>2</sub> formation path, was larger than those for  $\beta$  sites, i.e. E/Z-CH<sub>3</sub>NHNH and (CH<sub>3</sub>)<sub>2</sub>NNH formation paths. The product-specific rate coefficients were calculated using the canonical variational transition state theory with the small-curvature tunneling corrections in the temperature range of 200 - 2000 K. The overall rate coefficients were in good agreement with those measured by Vaghjiani (1995 and 1997), and that for N<sub>2</sub>H<sub>4</sub> + H calculated by Li et al. (2003). In the case of CH<sub>3</sub>NHNH<sub>2</sub> + H and  $(CH_3)_2NNH_2$  + H reactions, the dominant products at 300 K were found to be  $CH_3NNH_2$  + H<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>NNH + H<sub>2</sub>, respectively. Although the H abstraction paths from methyl group were negligible at around 300 K, their rate coefficients had larger temperature dependencies than the other channels and become compete at the higher temperature. At 2000 K, the branching ratio for these paths, i.e.  $CH_2NHNH_2 + H_2$  and  $CH_2N(CH_3)NH_2 + H_2$ , were predicted to be 0.25 and 0.49, respectively.

This work was supported by Grants-in-Aids for Scientific Research (C) Grant Number 19K04247, JSPS, Japan.

#### References

Li, QS., Zhang, X., and Zhang, SW. Direct Dynamics Study on the Hydrogen Abstraction Reaction  $N_2H_4 + H \rightarrow N_2H_3 + H_2$ . J Phys Chem A 2003;107:6055–6061.

Vaghjiani, GL. Laser photolysis studies of hydrazine vapor: 193 and 222-nm H-atom primary quantum yields at 296 K, and the kinetics of  $H + N_2H_4$  reaction over the temperature range 222–657 K. Int J Chem Kinet 1995;27:777–790.

Vaghjiani, GL. UV absorption cross sections, laser photodissociation product quantum yields, and reactions of H atoms with methylhydrazines at 298 K. J Phys Chem A 1997;101:4167–4171.

<sup>\*</sup>Corresponding author: kanno@meijo-u.ac.jp

## GAS-PHASE KINETICS AND PRODUCT STUDY OF THE CI REACTION WITH TRANS-2-METHYL-2-BUTENAL

Alberto García-Sáez<sup>1,2</sup>, María Antiñolo<sup>1,2</sup>, María Asensio<sup>1</sup>, José Albaladejo<sup>1,2</sup> and Elena Jiménez<sup>1,2,\*</sup> <sup>1</sup>Departamento de Química Física, Facultad de Ciencias y Tecnologías Químicas, Universidad de Castilla-La Mancha, Avda. Camilo José Cela 1B, 13071 Ciudad Real, SPAIN <sup>2</sup>Instituto de Investigación en Combustión y Contaminación Atmosférica, Edificio Polivalente, Camino de Moledores s/n, 13071 Ciudad Real, SPAIN

Keywords

Atmospheric chemistry, Cl oxidation, unsaturated aldehyde.

Carbonyl compounds are volatile organic compounds (VOCs) emitted to the troposphere by several natural sources and the by on-road traffic (Kawamura et al., 2000). In addition, they can be generated through the oxidation of other VOCs present in the troposphere. For example, unsaturated branched aldehydes have been reported, among others, as oxidation products of isoprene, which is one of the most emitted biogenic hydrocarbons. Up to date, there have been multiple studies on the gas-phase reactivity of unsaturated oxygenated compounds with tropospheric oxidants such as hydroxyl (OH) radicals or O<sub>3</sub>, but kinetic data on the reaction initiated by chlorine (Cl) atoms are scarce (see e.g. Jiménez and Barnes, 2015). Cl atoms are important in coastal and industrial areas and can have a profound impact on the tropospheric oxidation of VOCs because of their faster reactivity than that for OH radicals.

In particular, we have studied the kinetics and the formation of products in the Cl+*trans*-2methyl-2-butenal reaction. We report, for the first time, the rate coefficient of the title reaction at  $298 \pm 2$  K and  $760 \pm 5$  Torr using clean air as bath gas in a free NOx environment. A 16-L White-type cell coupled to a FTIR spectrometer was used in the relative kinetic experiments (Ballesteros et al., 2017). The photochemical reactor is surrounded by 4 actinic lamps and the reference compounds used were cyclohexane and isoprene. Gas-phase products were detected and quantified using the same setup and experimental conditions. The reaction mechanism has been proposed based on the observed products. Moreover, the formation of secondary organic aerosols (SOA) has been evaluated by detecting the new particles formed in the title reaction with a Fast Mobility Particle Sizer (FMPS) spectrometer. Finally, the implications of the atmospheric degradation of *trans*-2-methyl-2-butenal will be discussed in terms of its tropospheric lifetime and oxidation products.

#### References

Jiménez E, Barnes I. Daytime atmospheric chemistry of  $C_4$ – $C_7$  saturated and unsaturated carbonyl compounds. Hdb Env Chem 2015;32:53-104.

Kawamura K, Steinberg S, Kaplan, IR. Homologous series of  $C_1$ – $C_{10}$  monocarboxylic acids and  $C_1$ – $C_6$  carbonyls in Los Angeles air and motor vehicle exhausts. Atmos Environ 2000;34:4175-4191.

Ballesteros B, Jiménez E, Moreno A, Soto A, Antiñolo M, Albaladejo J. Atmospheric fate of hydrofluorolefins,  $C_xF_{2x+1}CH=CH_2$  (x=1,2,3,4 and 6): Kinetics with Cl atoms and products. Chemosphere 2017;167:330-343.

\*Corresponding author: elena.jimenez@uclm.es

## HIGHLY OXYGENATES MOLECULES FORMED BY OXIDATION OF TERPENES IN A JET-STIRRED REACTOR

N. Belhadj<sup>1,2</sup>, R. Benoit<sup>1</sup>, P. Dagaut<sup>1,\*</sup>, G. Dayma<sup>1,2</sup>, M. Lailliau<sup>1,2</sup> and Z. Serinyel<sup>1,2</sup> <sup>1</sup>CNRS-INSIS, Institut de Combustion, Aérothermique, Réactivité et Environnement 1C, Avenue de la recherche scientifique, 45071 Orléans cedex 2, FRANCE <sup>2</sup>Université d'Orléans, 6 Avenue du Parc Floral, 45100 Orléans, FRANCE

Keywords

Ketohydroperoxides, Terpenes, Oxidation, Mass spectrometry, HOMs.

With the growing interest for biomass-derived fuels the understanding of the combustion chemistry of terpenes becomes of major scientific importance. Terpenes have been proposed as biofuels for aviation because of their high energy density. They usually develop cool flames below 800 K. Very complex processes occur there, with the formation of peroxides intermediates such as ketohydroperoxides and highly oxidized molecules (HOMs) containing both hydroperoxy and carbonyl groups. Such chemicals are relatively unstable and difficult to analyze.

We studied the low-temperature oxidation of alpha-pinene, beta-pinene, and limonene ( $C_{10}H_{16}$ ) in a jet-stirred reactor. The experimental conditions were selected to maximize the production of ketohydroperoxides. We oxidized 5000 ppm of these three terpenes at 1 bar, T = 590 K, an equivalence ratio of 0.5, and at a residence time of 1 s. High-resolution mass spectrometry analyses were performed on solubilized products of terpenes oxidation in cooled acetonitrile.

The samples were analyzed using soft HESI electrospray ionization (+/-) and an Orbitrap® mass spectrometer (resolution: 140,000, mass accuracy <0.5 ppm RMS). The formation of ketohydroperoxides and highly oxygenated compounds resulting from third O<sub>2</sub> addition on the fuels primary radical (R) was observed:  $R + O_2 \leftrightarrows RO_2 \oiint QOOH$ ;  $QOOH + O_2 \oiint OOQOOH \leftrightarrows$ HOOQ'OOH followed by HOOQ'OOH +  $O_2 \leftrightarrows (HOO)_2Q'OO \leftrightarrows (i) (HOO)_2POOH \rightarrow OH +$ (HOO)<sub>2</sub>P=O (i.e., C<sub>10</sub>H<sub>14</sub>O<sub>5</sub>) and (ii) (HOO)<sub>2</sub>POOH +  $O_2 \rightarrow (HOO)_3POO \leftrightarrows (HOO)_3P'OOH \rightarrow OH$ + (HOO)<sub>3</sub>P=O (i.e., C<sub>10</sub>H<sub>14</sub>O<sub>7</sub>). Fourth oxygen addition yielding C<sub>10</sub>H<sub>14</sub>O<sub>9</sub> was also observed in the present work. Hydrogen–Deuterium exchange reactions using D<sub>2</sub>O were used to confirm the presence of –OH groups in the products.

Acknowledgements: Funding from Région Centre Val de Loire, FEDER, CPER PROMESTOCK, and the Labex Caprysses (ANR-11-LABX-0006-01) is gratefully acknowledged.

### MASS SPECTROMETRIC STUDY OF PROCESSES OF HALOGEN-CONTAINING ACIDS IN GAS AND WATER

Evgenii Vasiliev, Igor Morozov<sup>\*</sup>, Grigory Karpov, Nikolai Volkov

Semenov Institute of Chemical Physics RAS, Kosygin str. 4, 119991 Moscow, Russia

Halogenated acetic acids, are frequently encountered in environment; they were detected in atmospheric air, rain water, soil, surface and subsoil waters, and natural reservoirs. Trichloroacetic (TCA), Dichloroacetic (DCA), Monochloroacetic (MCA) acids a hazardous compound which has a negative effect on environment and live organisms, was found in environmental waters, air and biosphere. In the present work the rate constant of the gas-phase reaction of TCA, DCA with F-atoms was determined at T = 293 K using a relative rate method. In laboratory studies, reactions of F-atoms present a convenient method to generate radicals which can play role in atmospheric chemistry. The kinetic study of the reaction of TCA with Fatom consisted of four sets of experiments with different reference reactions. The reactions took place in a low-pressure flow reactor with mass-spectrometric monitoring of reagent concentrations. The reaction rate constant obtained was  $k = (4.4 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ <sup>1</sup>. This is an average value determined by relative method employing four reference reactions of F-atoms: with 1,1,1-trichloroethane, ethanol, cyclohexane, and 2-fluoroethanol, for which rate constant ratios  $k/k_{ref} = 7.4 \pm 1.2$ ,  $0.24 \pm 0.02$ ,  $0.28 \pm 0.02$  and  $0.34 \pm 0.04$ , respectively, were obtained. The resultant rate constant is compared with the rate constants for the related fluorosubstituted acids.



Another important issue of atmospheric chemistry relates to the behavior of acids in water. Mass spectra of aqueous solutions of monochloroacetic, dichloroacetic and trichloroacetic acids were obtained by electrospraying their aqueous solutions. It has been found that the mass spectra contain an acidic residue surrounded by several water molecules. Mass spectrum consists of a series of hydrated acid radical ions and degradation products in this series during electrospray. Three types of decay are observed: the detachment of water molecules from the outer sphere of the hydrated shell of the ions of the acid residue and the decomposition of the ions of the acidic residue with the break of the C-Cl and C-C bonds.

#### References

1. Vasiliev ES, Knyazev VD, Karpov GV, Morozov II, J. Phys. Chem. A, 2014, 118, 4013–4018.

2.Karpov GV,Vinogradova OA,Vasiliev ES,Morozov II,Rus.J.Phys.Chem.B,**2018**,12,4,684–689.

#### Acknowledgments

The work was supported by the program 0082-2014-008, № AAAA-A17- 117040310008-5 of the Ministry of Science and Higher Education of RF.

Corresponding author: morozov@chph.ras.ru

## KINETIC DISSOLUTION, VALIDATION, STATISTICAL MODELS OF A NEW GENERIC TABLETS OF LORATADINE.

Guermouche Saliha<sup>1</sup>

<sup>1</sup>Laboratoire de Chromatographie, Faculté de Chimie, USTHB, BP 32, El-Alia, Bab-Ezzouar, 16133 Alger, Algérie.

Keywords

Loratadine,	HPLC,	Dissolution,	Validation,	Statistical	models.
-------------	-------	--------------	-------------	-------------	---------

Comparative dissolution testing is extensively used as a tool to evaluate equivalency between oral solid dosage forms. Loratadine, ethyl-4-(8-chloro-5,6 dihydro-11H-benzo[5,6] cyclohepta [1,2 b] pyridin-11-ylidene)-1-piperidine carboxylate, is a second generation antihistamine drug closely structurally related to tricyclic antidepressants such as imipramine. Loratadine is selective peripheral H1receptor antagonists, devoid of any substantial effect on the central and autonomic nervous system (Graul and al., 2000).

A local generic preparation of tablets of this active ingredient was submitted to dissolution testing. Dissolution medium was a solution of 0.1 N hydrochloric acid; 900 mL, temperature  $37^{\circ}$ C. HPLC was choosen as analytic method, dissolution time was fixed to 60 minutes. The HPLC method involves separation on Hypersil C18 column using mixture of 40% acetonitrile and 60% of (methanol:H<sub>2</sub>O:phosphoric acid:ammonium dihydrogen phosphate) (220:300:2:3 g) (V/V/V/W) as mobile phase flowing at 2 ml/min and detection at 247 nm. The quantitative analysis of the data obtained from dissolution tests is deeper when mathematical formulas that express the dissolution results as a function of some characteristics of the dosage forms are used. In some cases, these mathematic models are derived from the theoretical analysis of the release process. In most of the cases a mechanistic expression is not available and some empirical equations have proven to be suitable (Costa et al., 2001). Mathematical dissolution models tested were, Zero and First order kinetics, Higuchi and Weibull model. The last model cited (Weibull) gave the data which complied with the experimental values of the dissolution testing after linearisation of its equation which is :

$$\frac{Q_t}{Q_{\infty}} = \left(1 - e^{-(k_d t)^{\beta}}\right)$$

Where  $Q_t$  is the accumulated mass is dissolved at time t and  $Q_{\infty}$  is the mass dissolved at infinite time,  $k_d \beta$  are a shape parameters that can also indicate the release mechanism.

#### References

Graul A, Leeson PA, Castaoer J, Drug Future 25 (2000) 339–346. Costa P, SousaJM, Lobo JM, Eur J Pharm Sci, 13 (2001) 123-133.

## Formaldehyde from a Chemical Source for Detection and Calibration with Laser-Induced Fluorescence

Christian Kühn and Matthias Olzmann<sup>\*</sup> Institut für Physikalische Chemie, Karlsruher Institut für Technologie (KIT), Kaiserstr. 12, 76131 Karlsruhe, Germany

Keywords

Formaldehyde, Laser-Induced Fluorescence, Calibration

Formaldehyde ( $CH_2O$ ) is an important species in atmospheric and combustion chemistry. Accordingly, there is much interest in methods for the qualitative detection of  $CH_2O$  and for a time-resolved determination of its concentration in reactive environments.

In our poster contribution, we first report on the detection of  $CH_2O$  as a product of the  $C_2H_4 + OH$  reaction. Here, OH was produced by pulsed laser photolysis of  $HNO_3$  at 248 nm, and the reaction product  $CH_2O$  was detected with laser-induced fluorescence (LIF). A LIF excitation spectrum of  $CH_2O$  produced from  $C_2H_4 + OH$  was recorded and verified by comparison with a LIF excitation spectrum of  $CH_2O$  produced from thermal decomposition of paraformaldehyde. As the latter method turned out unsuitable to obtain stable  $CH_2O$  concentrations for calibration, a second chemical system producing  $CH_2O$  was studied.

We chose a reaction system that was already used to obtain well-characterized HO<sub>2</sub> and OH radical concentrations (Dillon et al., 2012). The reaction mixture consists of  $Cl_2$ ,  $CH_3OH$ ,  $O_2$ , and NO, and the reaction sequence is initiated by pulsed laser photolysis of  $Cl_2$  at 351 nm:

 $Cl_{2} + h\nu \rightarrow Cl + Cl$   $Cl + CH_{3}OH \rightarrow CH_{2}OH + HCl$   $CH_{2}OH + O_{2} \rightarrow CH_{2}O + HO_{2}$   $(HO_{2} + NO \rightarrow NO_{2} + OH)$ 

We tested whether this system can also be used as a chemical source for formaldehyde giving well-characterized concentrations. In our work-in-progress poster, we present experimental and modeling results for this reaction system and discuss the influence of different parameters as well as general advantages and disadvantages of this method.

#### References

Dillon TJ, Pozzer A, Vereecken L, Crowley JN, Lelieveld J. Does acetone react with HO<sub>2</sub> in the upper-troposphere? Atmos Chem Phys 2012;12:1339-1351.

# Oxidation of methyl-substituted benzenes: Experimental and theoretical investigations of initiation reactions

Sommy Kounlavong, Naoto Izumi, Yu Sasaki, and Tatsuo Oguchi\* Toyohashi Univ. of Tech., Hibarigaoka, Tempaku-cho, Toyohashi, Aichi, JAPAN

Keywords

Combustion Chemistry, Low temperature oxidation, Aromatics, Pressure dependence.

The reaction of toluene ( $C_6H_5CH_3$ ) and related methyl-substituted benzenes (xylenes and trimethyl-benzenes) with hydroxyl radical (OH) are important in the oxidation process of mixed hydrocarbons fuels. The literature shows strange temperature dependence of rate coefficients (Baulch et al., 2005). The mechanism of those reactions are explained here (in the case of toluene):

 $\begin{array}{cccc} C_{6}H_{5}CH_{3}+OH \rightarrow & C_{6}H_{5}(OH)CH_{3} & (T < 400 \text{ K}) & (1a) \\ \rightarrow & C_{6}H_{5}CH_{2}+H_{2}O & (T > 400 \text{ K}) & (1b) \\ \rightarrow & C_{6}H_{4}CH_{3}+H_{2}O & (T > 400 \text{ K}) & (1c). \end{array}$ 

Experimental investigation and theoretical analysis for high-temperature region was found for this reaction (Seta et al., 2006), however, detail theoretical analysis and experimental investigation of pressure dependences for another methyl substituted benzenes are not found in literature.

In this study, rate coefficients of the title reaction were obtained from the condition of pseudo first order reaction of OH radicals against methylbenzenes. Also, detail theoretical analysis including computational investigation of potential energy surfaces which does not have definite transition states was performed. Reaction rate coefficients were also calculated by using transition state theory.

In the 1,2,4-trimethylbenzene(124TMB)'s case, there are three different methyl groups in a molecule. The differences of bonding energy between C-H bonds were very small (<1.4 kJ mol<sup>-1</sup>). However, reaction energy barrier for the abstraction reaction of H atom with OH were slightly different between the isolated methyl group and neighboring-dimethyl group. Therefore, practical rate coefficients are also different so that it should be considered to build reaction models. The differences between the three C-H bonds in a benzene group of 124TMB were also examined, and small differences (<1.7 kJ mol<sup>-1</sup>) were obtained. In conclusion, site-selectivity between the C-H bonds of benzene group in the 124TMB can be ignored in the reaction scheme, however, H-abstraction from neighboring-dimethyl groups such as o-xylene or 124TMB are important rather than isolated methyl groups.

#### References

Baulch DL et al., Evaluated Kinetic Data for Combustion Modeling: Supplement II, J. Phys. Chem. Ref. Data, 2005:34:757.

Seta T, Nakajima M, and Miyoshi A, J. Phys. Chem. A 2006 :110 :5081.

## GAS PHASE KINETIC AND THEORETICAL APPROACH ON THE CHLORINE ATOM CHEMISTRY OF EPOXIDES

### <u>Carmen Tovar<sup>1</sup></u>, Alexander Haack<sup>1</sup>, Ian Barnes<sup>1</sup>, Iustinian Bejan<sup>2</sup>, Peter Wiesen<sup>1,\*</sup>

<sup>1</sup> Institute for Atmospheric and Environmental Research, University of Wuppertal, 42119 Wuppertal, Germany

<sup>2</sup> "Alexandru Ioan Cuza" University of Iasi, Faculty of Chemistry and Integrated Center of Environmental Science Studies in the North-Eastern Region – CERNESIM, 700506, Iasi, Romania

#### Keywords

epoxides, reactivity trends, SAR, chlorine kinetics, theoretical approach

Epoxides are the simplest oxygen-containing heterocyclic class of volatile organic compounds (VOC) also known as cyclic ethers. They are well known products formed from chemical degradation of biogenic VOCs and biomass derived alcohols. The anthropogenic formation of cyclic ethers comprise the initial reactions of alkyl radicals with oxygen in combustion and precombustion processes with a significant release of the oxygenated pollutants as found in the exhaust gases of engines (Auzmendi-Murua and Bozelli, 2014). To date little is known about the gas phase chemistry of epoxides and the kinetic investigations from this study could bring a significant step forward for understanding of their behaviour in atmosphere.

Gas phase kinetic rate coefficients have been investigated at 298±2 K and atmospheric pressure of synthetic air for the reaction of chlorine atoms with cyclohexene oxide (CHO), 1,2-epoxyhexane (EHX), 1,2-epoxybutane (12EB), *trans*-2,3-epoxybutane (*t*EB) and *cis*-2,3-epoxybutane (*c*EB). The measurements were performed at Wuppertal laboratories in a 1080 *l* Quartz Reactor (QUAREC) and a 480 *l* Duran glass chamber using long path *in situ* FTIR spectroscopy. The following average rate coefficients (in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) were obtained in this study:  $k_{(Cl+ CHO)} = (2.40\pm0.87) \times 10^{-10}$ ,  $k_{(Cl+ EHX)} = (1.77\pm0.63) \times 10^{-10}$ ,  $k_{(Cl+ 12EB)} = (8.43\pm2.55) \times 10^{-11}$ ,  $k_{(Cl+ cEB)} = (6.92\pm2.15) \times 10^{-11}$ ,  $k_{(Cl+ tEB)} = (6.99\pm2.09) \times 10^{-11}$  using at least two reference hydrocarbon for each epoxy compound investigated. Experiments have been performed in one of the reactors with the exception of *c*EB whose rate coefficient value is an average of experimental data obtained in both chambers.

The kinetic data obtained in this study proved that the consecutive addition of a  $CH_2$  group to aliphatic chain of the propylene oxide increases the reactivity of the epoxy compounds towards chlorine atom reaction. Theoretical calculations performed in this study enhanced our experimental findings and provide interesting information about the branching fractions of the hydrogen abstraction reaction and reactivity trends for these compounds. This is to our knowledge the first kinetic and theoretical study of the reaction of these compounds with chlorine atoms.

#### References

Auzmendi-Murua I and Bozelli J, Thermochemical Properties and Bond Dissociation Enthalpies of 3-to 5-Member Ring Cyclic Ether Hydroperoxides, Alcohols, and Peroxy Radicals: Cyclic Ether Radical+3O2 Reaction Thermochemistry *J. Phys. Chem. A* 2014: 118: 17, 3147-3167.

#### Acknowledgement:

The authors acknowledge financial support from European grant EUROCHAMP-2020, I. Bejan acknowledges the UEFISCDI grant PN-III-P4-ID-PCE-2016-0807, and C. Tovar acknowledges the FANTEL fellowship.

## EXPERIMENTAL AND THEORETICAL DETERMINATION OF DMC/AIR FLAME VELOCITIES

S. de Persis<sup>1,2</sup>, N.Chaumeix<sup>1</sup>, Y.Fernandes<sup>1,2,3</sup>, A. Bry<sup>3</sup>, A. Comandini<sup>1</sup> <sup>1</sup>CNRS-INSIS, Institut de Combustion, Aérothermique, Réactivité et Environnement 1C, Avenue de la recherche scientifique, 45071 Orléans cedex 2, FRANCE <sup>2</sup>Université d'Orléans, 6 Avenue du Parc Floral, 45100 Orléans, FRANCE <sup>3</sup>CEA, Le Ripault, BP 16, 37260, Monts, France

Keywords

Flame velocities, Spherical Bomb, dimethylcarbonate

Dimethylcarbonate (DMC) is used in many applications (as an organic raw material, as a solvent electrolyte in lithium-ion batteries or as a fuel additive) and therefore the assessment of its safety is mandatory. To assess the risk of DMC/O<sub>2</sub>/N<sub>2</sub> mixtures, it is necessary to characterize their fundamental combustion properties. This is the aim of the present study, which presents new experimental data on the combustion of DMC/air mixtures. Laminar flame speeds have been measured using the outward spherical propagation configuration [Goulier (2016), Nativel (2016)] for three initial temperatures (318, 363 and 423 K) at an initial pressure of 1.013 bar. The equivalence ratio was varied from 0.7 to 1.5. The experimental laminar flame velocities were compared to the DMC/air flame velocity measurements performed by Bardin et al. (2013) in a heat flow burner. A fairly good agreement was found. Three detailed kinetic mechanisms from the literature (Glaude (2005), Sun (2016) and Alexandrino (2018)) were used to simulate the experimental results using Chemical Workbench4.2. A large discrepancy was found comparing the results from different mechanisms, as well as between the simulated data and the experimental ones. The best agreement was obtained with the mechanism of Alexandrino et al. as shown for instance in figure 1 (at 318K).



#### References

Alexandrino K, Alzueta MU, Curran HJ, Combustion and Flame, 188, 212–226 (2018)

Bardin ME, Ivanov, EV, Nilsson, EJK, Vinokurov VA and Konnov AA, *Energy and Fuels*, 27, 5513–5517 (2013)

CWB Comput Mater Sci 2003; 28:169–78; http://www.kintechlab.com/products/chemical-workbench/. Chemical Workbench v.4.2.

Glaude PA, Pitz WJ, Thomson MJ, Proc. Combust. Inst., 30, 1111–1118 (2005).

Goulier J, Bizon K, Chaumeix N, Meynet N, Continillo G, AIP Conference Proceedings, 1790, 110006, (2016).

Nativel D, Pelucchi M, Frassoldati A, Comandini A, Cuoci A, Ranzi E, Chaumeix N, Faravelli T, Combustion and Flame, 166, 1-18 (2016)

Sun W, Yang B, Hansen N, Westbrool CK, Zhang F, Wang G, Moshammer K, Law CK, Combustion and Flame, 164, 224–238, (2016)

## **ROOOH : A SOURCE OF INTERFERENCE FOR OH MEASUREMENTS IN LOW NO ENVIRONMENTS**

Christa Fittschen<sup>1</sup>, Mohamed AlAjami<sup>1</sup>, Sebastien Batut<sup>1</sup>, Valerio Ferracci<sup>2,3</sup>, Scott Archer-Nicholls<sup>2</sup>, Alexander T. Archibald<sup>2,4</sup>, Coralie Schoemaecker<sup>1</sup> <sup>1</sup>CNRS-Université de Lille, PhysicoChimie des Processus de Combustion et de l'Atmosphère, Cité Scientifique, Bât. C11, 59655 Villeneuve d'Ascq, FRANCE <sup>2</sup>University of Cambridge, Centre for Atmospheric Science, Cambridge, CB21EW, UK <sup>3</sup>Cranfield University, Centre for Environmental and Agricultural Informatics, Cranfield MK43 0AL, UK <sup>4</sup>National Centre for Atmospheric Science, Cambridge, UK

Keywords: Atmospheric chemistry, OH radicals, Radical measurements, remote environments

Filed campaigns have been carried out with the FAGE technique in remote biogenic environments in the last decade to quantify the in situ concentrations of OH, the main oxidant in the atmosphere. These data have revealed concentrations of OH radicals up to a factor of 10 higher than predicted by models, whereby the disagreement increases with decreasing NO concentration. This was interpreted as a major lack in our understanding of the chemistry of biogenic VOCs, particularly isoprene, which are dominant in remote pristine conditions. But interferences in these measurements of unknown origin have also been discovered for some FAGE instruments: using a pre-injector, all ambient OH is removed by fast reaction before entering the FAGE cell, and any remaining OH signal can be attributed to an interference. This technique is now systematically used for FAGE measurements, allowing the reliable quantification of ambient OH concentrations along with the signal due to interference OH. However, the disagreement between modelled and measured high OH concentrations of earlier field campaigns as well as the origin of the now-quantifiable background-OH is still not understood.

We present the compelling idea that this interference, and thus the disagreement between model and measurement in earlier field campaigns, might be at least partially due to the unexpected decomposition of a new class of molecule, ROOOH, within the FAGE instruments. This idea is based on experiments, obtained with the FAGE set-up of University Lille, and supported by a modelling study. Even though the occurrence of this interference will be highly dependent on the design and measurement conditions of different FAGE instruments, including ROOOH in atmospheric chemistry models might reflect a missing piece of the puzzle in our understanding of OH in clean atmospheres.

#### References

Fittschen, C., Al Ajami, M., Batut, S., Ferracci, V., Archer-Nicholls, S., Archibald, A.T., Schoemaecker, C.: ROOOH: a missing piece of the puzzle for OH measurements in low NO environments? ACP; 2019, 19, 349-362

### Development of a stagnation plate burner as a new support to study cool flame chemistry

## Nabil MOKRANI<sup>\*</sup>, Thomas PANAGET, Sébastien BATUT, Laure PILLIER and Guillaume VANHOVE

## Univ. Lille, CNRS, UMR 8522 -PC2A -Physicochimie des Processus de Combustion et de l'Atmosphère, F-59000 Lille, France

#### Keywords

Stagnation plate burner, Cool flame, CH<sub>2</sub>O-PLIF, Low Temperature combustion

The new concepts of ignition and combustion based on fuel-lean, exhaust gas-diluted operation, allowing lower fuel consumption and pollutant emissions, represent a challenge for future thermal engines, and call for dedicated research work. To contribute to the development of engine concepts such as Spark-Assisted Compression ignition (SACI), Partially Premixed Compression Ignition (PPCI), Reactivity Controlled Compression Ignition (RCCI), and Gasoline Compression ignition (GCI) through low-temperature combustion kinetic studies, a new stagnation plate burner has been developed at the PC2A laboratory.

This device allows the stabilization of ozone-seeded cool flames at atmospheric pressure, in a large range of equivalence ratios, strain rates and  $O_3$  mole fractions, its feasability having been demonstrated with DiMethylEther as the fuel (DME) (Mokrani et al. 2019). Through a further study, CH<sub>2</sub>O Planar Laser Induced Fluorescence (PLIF) and CH<sub>2</sub>O\* chemiluminescence imaging were used to locate the flame front position and investigate the axial structure of the stabilized cool flames, demonstrating axisymmetric geometry of the stabilized cool flames. This configuration therefore allows kinetic investigation of low-temperature combustion mechanisms in steady, non-diluted conditions, through the implementation of advanced diagnostics and chemical analysis techniques.

The relative CH<sub>2</sub>O mole fraction axial profiles extracted from the PLIF measurements, as well as extinction limits of the strained flames were used for comparison with simulations using different kinetic mechanisms available in the literature (Aramco 1.3 (Metcalfe et al. 2013), Aramco 2.0 (Heufer et al. 2013), HP-mech v1.8-no-NOx (Reuter et al. 2018) and Wang model (Wang et al. 2015)), an ozone sub mechanism (Halter et al. 2011) being added.

#### References

- Halter et al. 2011. "Experimental and Detailed Kinetic Modeling Study of the Effect of Ozone on the Combustion of Methane." *Energy and Fuels* 25(7): 2909–16.
- Heufer, Karl A. et al. 2013. "An Experimental and Detailed Chemical Kinetic Modeling Study of Hydrogen and Syngas Mixture Oxidation at Elevated Pressures." *Combustion and Flame* 160(6): 995–1011.
- Metcalfe, Wayne K., Sinéad M. Burke, Syed S. Ahmed, and Henry J. Curran. 2013. "A Hierarchical and Comparative Kinetic Modeling Study of C1 - C2 Hydrocarbon and Oxygenated Fuels." *International Journal of Chemical Kinetics* 45(10): 638–75.
- Mokrani et al. 2019. "Experimental Study of Premixed Ozone-Seeded DME / O 2 Cool Flames on a Stagnation Plate Burner." *9th European Combustion Meeting*.
- Reuter, Christopher B. et al. 2018. "Counterflow Flame Experiments and Chemical Kinetic Modeling of Dimethyl Ether/Methane Mixtures." *Combustion and Flame* 196: 1–10. https://doi.org/10.1016/j.combustflame.2018.06.004.
- Wang, Zhandong et al. 2015. "Experimental and Kinetic Modeling Study of the Low- and Intermediate-Temperature Oxidation of Dimethyl Ether." *Combustion and Flame* 162(4): 1113–25. http://dx.doi.org/ 10.1016/j.combustflame.2014.10.003.

## LOW PRESSURE REACTION KINETICS OF OH+HNO<sub>3</sub> IN AN EXTENDED TEMPERATURE RANGE

Yuri Bedjanian<sup>1\*</sup>, A.R. Ravishankara<sup>2</sup>

<sup>1</sup>CNRS-INSIS, Institut de Combustion, Aérothermique, Réactivité et Environnement 1C, Avenue de la recherche scientifique, 45071 Orléans cedex 2, FRANCE
<sup>2</sup>Departments of Chemistry and Atmospheric Science, Colorado State University 1872 Campus Delivery, Fort Collins, CO 80523-1872, USA

Keywords

OH radicals, nitric acid, rate constant, atmospheric chemistry.

The reaction of OH with  $HNO_3$  is an important atmospheric process that impacts stratospheric ozone and  $HO_x$  budget as well as  $NO_x$  partitioning in UTLS. It's kinetics has been subject to many studies but not at higher temperatures and low pressures. We have studied this reaction using a low-pressure discharge flow reactor combined with an electron impact ionization mass spectrometer using helium and nitrogen as bath gases in the pressure range (0.56-8.2) Torr and temperatures between 217 and 695 K. Our results are shown below.



Pressure and temperature (U-shaped) dependence of the reaction rate constant suggests the presence of two competing pathways. These results will be discussed in light of the reaction mechanism and in comparison with previous higher pressure data and parametrizations of the rate constant for atmospheric modeling.

\*Corresponding author: yuri.bedjanian@cnrs-orleans.fr

## **REACTIVITY OF NO<sub>3</sub> RADICAL WITH MONOTERPENES: THEORETICAL APPROACH FOR MECHANISTIC STUDY**

M.-T. Rayez<sup>1,\*</sup>, M. Cirtog<sup>2</sup>, J.- C. Rayez<sup>1</sup>, A. Fouqueau<sup>2</sup> and B. Picquet-Varrault<sup>2</sup>

<sup>1</sup>Université de Bordeaux, Institut des Sciences Moléculaires, UMR-CNRS 5255, 351 cours de la libération, 33405 Talence, FRANCE <sup>2</sup>Université de Paris-Est Créteil et Paris Diderot, Laboratoire Interuniversitaire des Systèmes Atmosphériques, UMR-CNRS 7583, 61 avenue du Général de Gaulle, 94010 Créteil, FRANCE

#### Keywords :

NO<sub>3</sub>, monoterpènes, reactivity, quantum chemical calculations, DFT method

Biogenic Volatile Organic Compounds (BVOCs) are highly emitted by vegetation and play a key role in atmospheric chemistry (*Atkinson and Arey*, 2003). They are very reactive with atmospheric oxidants (OH, NO<sub>3</sub>, O<sub>3</sub>) and significantly contribute to the formation of Secondary Organic Aerosol (SOA) at the global scale (*Brown and Stutz*, 2012)]. In addition, night-time chemistry initiated by NO<sub>3</sub> radicals leads to the formation of Organic Nitrates (ON) which behave as reservoirs for reactive nitrogen. However, the reactivity of NO<sub>3</sub> radical with BVOCs other than isoprene and  $\alpha$ - and  $\beta$ -pinene, remains poorly understood.

Thus, the reactivity of NO<sub>3</sub> with three monoterpenes has been investigated based on complementary approaches: experiments in simulation chambers (LISA, Créteil) and quantum chemistry calculations (ISM, Bordeaux). We have focused our work on the three following monoterpenes:  $\gamma$ -,  $\alpha$ -terpinene and terpinolene since (i) they belong to the family of the 14 more emitted terpenes in the atmosphere (*Graedel*, 1978), (ii) they have similar structures (conjugated and non-conjugated as well as endo and exocyclic C=C double bonds) in order to investigate the influence of the structure on the reactivity and the reaction products and, (iii) they are very few documented in the literature (Ng et al., 2017).

We present here the theoretical approach of the mechanistic study. Quantum chemical calculations were performed with the GAUSSIAN 09 program package using Density Functional Theory (DFT) with the functional BH&HLYP and the 6-31+G(d,p) basis set in order to investigate the (1) alkyls stability and (2) alkoxyls evolution to help interpret the experimental results. The theoretical results will be discussed and thus compared with the experimental findings.

#### References

Atkinson R, Arey J. Atmos. Env. 2003; 37 Supplement No. 2, pp. S197-S219 Brown SS and Stutz J, Chem. Soc. Rev. 2012; 41; pp. 6405–6447 Graedel TE Chemical compounds in the Atmosphere, New-York, Academic Press: 1978. 440p Ng NL et al., Atmos. Chem. Phys. 2017; 17: 2103-2162

\*Corresponding author: marie-therese.rayez@u-bordeaux.fr

## First PEPICO Spectroscopy Investigations of n-Pentane Low Temperature Oxidation in a Jet-Stirred Reactor

Jérémy Bourgalais<sup>1</sup>, Frédérique Battin-Leclerc<sup>2,3</sup>, Olivier Herbinet<sup>2,3</sup>, Zhandong Wang<sup>4</sup>, Luc-Sy Tran<sup>5</sup>, Guillaume Vanhove<sup>5</sup>, Laurent Nahon<sup>6</sup>, Gustavo Garcia<sup>6</sup>

<sup>1</sup>LATMOS/IPSL, UVSQ Université Paris-Saclay, Sorbonne Université, CNRS, Guyancourt, France

<sup>2</sup>Université de Lorraine, Laboratoire Réactions et Génie des Procédés, UPR 3349, Nancy F-54000, France

<sup>3</sup>CNRS, Laboratoire Réactions et Génie des Procédés, UPR 3349, Nancy F-54000, France

<sup>4</sup>National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, People's Republic of China

<sup>5</sup>Physico-Chimie des processus de Combustion et de l'Atmosphère (PC2A), UMR 8522 CNRS, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq Cedex, France

<sup>6</sup>Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin-BP 48, 91192 GIF-sur-Yvette Cedex, France

Keywords

Combustion - Synchrotron Radiation - Electron Spectroscopy - Oxidation - Jet Stirred Reactor

In the last years, soft photoionization technique using synchrotron radiation was demonstrated as a powerful tool to monitor reactive intermediates produced by gas-phase chemical reactions or photodissociation processes. Coupled to photoelectron-photoion coincidence (PEPICO) spectroscopy, those experimental techniques are able to address a range of challenging problems including quantitative determination of isomers, detection of free radicals, and fragmentation of reactive species produced in pyrolysis or in combustion studies.

Consequently, in a well-known environment context where one of the major challenges is to improve combustion efficiency and reduce harmful pollutant emission, we investigated the gasphase oxidation of *n*-pentane in a jet-stirred reactor (JSR), for the first time, on the VUV DESIRS beamline at the SOLEIL synchrotron (France). Experimentally, the gas inside the JSR was sampled and crossed the VUV synchrotron radiation at the center of a double imaging photoelectron photoion coincidence (i2PEPICO) spectrometer. Then photoelectrons are velocity map imaged and detected according to their velocity on a fast position sensitive detector and by correlating threshold photoelectrons with ions from the same ionization event, photoion mass selected threshold photoelectron spectra are obtained.

JSR experiments were performed at temperatures ranging from 550 to 650 K and atmospheric pressure for different mixing ratios of fuel. The time-of-flight mass spectra obtained as a function of the photon energy exhibited all the m/z corresponding to the expected stable products, including diones and ketohydroperoxides (KHP), along with significant contribution of fragments potentially originating from KHP. Here, we present the current progress on structural identification of these masses based on the associated threshold photoelectron (TPE) spectra analysis.

<sup>\*</sup>Corresponding author: jeremy.bourgalais@latmos.ipsl.fr

### A theoretical study of pyrene formation from fluoranthene

D. Khiri<sup>1</sup>, Duy Quang Dao<sup>2</sup>, Thanh Binh Nguyen<sup>3</sup>, L. Gasnot<sup>1</sup>, F. Louis<sup>1</sup> and A. El Bakali<sup>1</sup> <sup>1</sup>Univ. Lille, CNRS, UMR 8522-PC2A, PhysicoChimie des Processus de Combustion et de l'Atmosphère, 59000 Lille, France

<sup>2</sup>Institute of Research and Development, Duy Tan University, 03 Quang Trung, Danang, 55000, Vietnam

<sup>3</sup>Faculty of Chemical Engineering, The University of Danang - University of Science and Technology, 54 Nguyen Luong Bang St., Danang, 55000, Vietnam

Keywords

Combustion; PAHs; isomerization; pyrene; fluoranthene; potential energy surface.

This work has investigated the reaction process concerning the pyrene formation from fluoranthene in their electronic ground states. Both the aromatic compounds are considered as direct soot precursors. The geometrical parameters, the vibrational frequencies and the zeropoint energies have been calculated using the BMK method and the 6-311++G(d,p) basis set. More accurate single-point energies have been obtained using the BMK/6-311++G(3df,2p) to retrieve thermodynamic properties ( $\Delta_r H^{\circ}(T)$  and  $\Delta_r G^{\circ}(T)$ ) over a wide temperature range (298–2500 K). The isomerization reaction of fluoranthene to pyrene is exothermic and spontaneous in standard conditions. The transition states and the possible intermediate species have been located on the singlet potential energy surface in order to determine the reaction mechanism. Implications for combustion chemistry are presented and discussed.



\* florent.louis@univ-lille.fr

## **Theoretical investigation of the reaction CI + HOIO**

S. Suliman<sup>1\*</sup>, S. Taamalli<sup>2</sup>, D. Khiri<sup>2</sup>, I. Cernusak<sup>1</sup>, L. Cantrel<sup>3</sup> and F. Louis<sup>2</sup>

<sup>1</sup>Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences,

Comenius University in Bratislava, Ilkovičova 6, 84215 Bratislava, Slovakia

<sup>2</sup>Univ. Lille, CNRS, UMR 8522-PC2A, PhysicoChimie des Processus de Combustion et de l´Atmosphère, 59000 Lille, France

<sup>3</sup>Institut de Radioprotection et de Sûreté Nucléaire (IRSN), PSN-RES, Cadarache, Saint-Paul Lez Durance 13115, France

#### Keywords

#### Atmosphere; Halogens; Reactivity; Quantum Chemistry

Chlorine gas is recognized to be an efficient ozone destroyer in the stratosphere. Its efficiency strongly depends on the chlorine partitioning between its active forms (CI, CIO) and inactive reservoir species (e.g. HCl or CIOOCI). Because of their possible implications in the destruction of the stratospheric ozone layer, chlorine oxides have drawn the attention of atmospheric chemists. Computational studies on HOIO species are scarce and it is only very recently that experimental evidence of iodous acid in the gas phase has been reported in the literature (Sipilä et al., 2016).

The main objective of this work to provide reliable kinetic and thermodynamic data for the gas phase reaction of iodous acid with chlorine atoms. Several possible reaction pathways are studied: H-abstraction, I-abstraction, OH-abstraction, IOabstraction. The reaction mechanism involves many stationary points on the potential energy surface and reveals some unusual features for the H-abstraction. Theoretical calculations were performed with the augmented correlation consistent basis sets augcc-pVTZ for H and O atoms, the aug-cc-pV(T+d)Z for Cl atom, and aug-cc-pVTZ-PP that incorporates a small-core (28 electrons) relativistic pseudo-potential for iodine. Single-point energies at the DFT structures were calculated using the CCSD(T) method and the weighted core-valence basis sets aug-cc-pwCVnZ (n = D, T, Q). Different corrections to the potential energies were furthermore calculated (CBS, ZPE, CV, SR, and SOC). Implications for atmospheric chemistry are presented and discussed.

#### References

M. Sipilä, N. Sarnela, T. Jokinen, H. Henschel, H. Junninen, J. Kontkanen, S.Richters, J. Kangasluoma, A. Franchin, O. Peräkylä, M.P. Rissanen, M. Ehn, H.Vehkamäki, T. Kurten, T. Berndt, T. Petäjä, D. Worsnop, D. Ceburnis, V.-M.Kerminen, M. Kulmala, C.D. O'Dowd, Molecular-scale evidence of aerosol particle formation via sequential addition of HIO<sub>3</sub>, Nature (2016) 1–3, http://dx.doi.org/10.1038/nature19314.

## Premixed flame structure of ethyl pentanoate: experimental study and chemical kinetic modeling

Artëm Dmitriev<sup>1,2</sup>, Ksenia Osipova<sup>1,2</sup>, Tatiana Bolshova<sup>1</sup>, Denis Knyazkov<sup>1,2</sup> and Pierre-Alexandre Glaude<sup>3</sup>

 <sup>1</sup>Voevodsky Institute of Chemical Kinetics and Combustion, Novosibirsk 630090, RUSSIA
 <sup>2</sup>Novosibirsk State University, Novosibirsk 630090, RUSSIA
 <sup>3</sup>Université de Lorraine, École Nationale Supérieure des Industries Chimiques de Nancy, Laboratoire Réactions et Génie des Procédés, UMR CNRS 7274, Nancy Cedex 54001, FRANCE

#### Keywords

Ethyl pentanoate, ethyl valerate, combustion, flat flame, flame sampling, chemical kinetics, reaction mechanism

Diversification of transportation fuels is a key option for sustainable transport. In this regard, particular attention is paid to pentanoic (valeric) esters since they could be produced from lignocellulose. Thus, chemical kinetic behavior of pentanoates in the combustion processes is of great fundamental and practical interest. Since methyl esters were studied more intensively than ethyl esters, ethyl pentanoate was chosen as a target compound. In this work, stoichiometeric premixed 1D flames of ethyl pentanoate at pressures 50 and 760 Torr were investigated. Flame sampling gas chromatography and molecular beam mass spectrometry were used to measure spatial distributions of mole fractions of various flame species, including key intermediates, at low and atmospheric pressure, respectively. A modernized detailed chemical kinetic mechanism for ethyl valerate combustion is elaborated using the well-known mechanism of Dayma (Dayma et al., 2012) and the recent mechanism of Sun (Sun et al., 2017) as a basis. The new mechanism was validated against the novel flame structure data and the data on laminar burning velocities from (Dayma et al., 2012). In comparison with the mechanism of Dayma, the new mechanism provided better prediction of mole fraction profiles of acetylene, allene, propyne, propane and some other short intermediates. However, several discrepancies were also observed. Predictions of laminar burning velocities appeared to be very close to those by the mechanism of Dayma. Comparative analysis of the mechanisms has shown, that the use of recent rate constants from (Sun et al., 2017) for reactions of Habstraction from the fuel molecule led to redistribution of primal pathways of fuel consumption in the new mechanism, thus the resulting pool of fuel radicals in the new mechanism differs noticeably from that in the mechanism of Dayma.

#### References

Dayma, G., Halter, F., Foucher, F., Togbé, C., Mounaim-Rousselle, C., Dagaut, P. Experimental and Detailed Kinetic Modeling Study of Ethyl Pentanoate (Ethyl Valerate) Oxidation in a Jet Stirred Reactor and Laminar Burning Velocities in a Spherical Combustion Chamber. Energy Fuels 2012;26:4735–4748.

## STUDY OF METHYL-3-HEXENOATE COMBUSTION KINETICS: MECHANISM DEVELOPMENT AND NEW DATA FOR ATMOSPERIC AND HIGH-PRESSURE CONDITIONS

Ilya Gerasimov<sup>1,3,\*</sup>, Denis Knyazkov<sup>3,4</sup>, Tatyana Bolshova<sup>3</sup>, Andrey Shmakov<sup>3,4</sup>, Oleg Korobeinichev<sup>3</sup>, Maxime Carbonnier<sup>1,5</sup>, Benoîte Lefort<sup>5</sup>, Alan Kéromnès<sup>5</sup>, Luis Le Moyne<sup>5</sup>, Zeynep Serinyel<sup>1,2</sup>, Guillaume Dayma<sup>1,2</sup>, Philippe Dagaut<sup>1</sup> <sup>1</sup>CNRS-INSIS, Institut de Combustion, Aérothermique, Réactivité et Environnement 1C, Avenue de la recherche scientifique, 45071 Orléans cedex 2, FRANCE <sup>2</sup>Université d'Orléans, 6 Avenue du Parc Floral, 45100 Orléans, FRANCE <sup>3</sup>Voevodsky Institute of Chemical Kinetics and Combustion, 630090 Novosibirsk, Russia <sup>4</sup>Novosibirsk State University, 630090 Novosibirsk, Russia <sup>5</sup>DRIVE, EA1859, Université de Bourgogne – Franche Comté, Nevers, France

#### Keywords

Methyl-3-hexenoate, Combustion kinetics, Flame structure.

Most biodiesel fuels produced by transesterification from vegetable oils contain unsaturated esters, which are difficult to remove completely. Recent investigations have shown that the presence of a double bond in the alkyl chain can considerably affect the chemical kinetics of its combustion and, the influence of the double bond remains a very important research topic. To understand and predict possible distinctions in combustion kinetics of saturated and unsaturated biodiesel components, a comprehensive study of methyl-3-hexenoate (MHX3D) oxidation was performed in different experimental conditions.

In this work, a development of kinetic mechanism for MHX3D oxidation originally tested against chemical speciation data in a jet-stirred reactor (JSR) at 10 atm (Zhang et al., 2014) is continued basing on the novel data for:

- 1) Chemical speciation in JSR at 1 atm for MHX3D/O<sub>2</sub>/N<sub>2</sub> mixtures with equivalence ratios  $\phi$ =0.6, 1 and 2 ICARE (Orléans, France);
- 2) Structure of stoichiometric premixed flame of MHX3D/O<sub>2</sub>/Ar stabilized on a flat burner at 1 atm studied by molecular-beam mass-spectrometry ICKC (Novosibirsk, Russia);
- 3) Ignition delay times measured behind reflected shock waves with an initial pressure of 20 and 40 bar and within a temperature range of 1100 1500 K for mixtures of MHX3D/O<sub>2</sub>/Ar (1% of MHX3d at  $\varphi = 0.6$ , 1.2 and 2.4) DRIVE Laboratory (Nevers, France).

Several modifications to the original mechanism were made to achieve reasonable predictions of all sets of experimental data. Importance of low-temperature oxidation reactions and pressure dependent rate constants of several reaction pathways is discussed. This study will serve as a basis for future improvement of chemical kinetic mechanisms for low temperature oxidation and combustion of unsaturated methyl esters with longer alkyl chains.

#### References

Zhang K, Togbé C, Dayma G, Dagaut P, Experimental and kinetic modeling study of transmethyl-3-hexenoate oxidation in JSR and the role of C=C double bond. Comb. Flame 161 2014;161:818–825.

## Shock Wave and Theoretical Modeling Study of the Dissociation of CH<sub>2</sub>F<sub>2</sub> – Primary and secondary reactions

Lars Sölter<sup>1,\*</sup>, Carlos J. Cobos<sup>2</sup>, Elsa Tellbach<sup>1</sup>, and Jürgen Troe<sup>1</sup> Institute for Physical Chemistry, University Göttingen, Tammannstr. 6, 37077 Göttingen, GERMANY <sup>2</sup> INIFTA, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, ARGENTINA

Keywords

reaction mechanism, kinetics, thermal decomposition.

The unimolecular dissociation of  $CH_2F_2$  leading to  $CF_2 + H_2$ , CHF + HF, or  $CHF_2 + H$ , is investigated by quantum chemical calculations and unimolecular rate theory. Modeling of the rate constants is accompanied by shock wave experiments over the range 1400-2200K.

Within the range of 1400 – 1800 K the formation of  $CF_2$  was monitored. It is shown that the energetically most favourable dissociation channel leading to  $CF_2 + H_2$  has a higher threshold energy than the energetically less favourable one leading to CHF + HF. Falloff curves of the dissociations are modeled. Under the conditions of the described experiments, the primary dissociation  $CH_2F_2 \rightarrow CHF + HF$  is followed by a reaction  $CHF + HF \rightarrow CF_2 + H_2$ . The experimental value of the rate constant of the latter indicates that this reaction does not proceed by an addition-elimination process involving  $CH_2F_2^*$  intermediates as assumed before.

Additionally, the thermal dissociation of  $CH_2F_2$  and the reaction of  $CF_2$  with  $H_2$  was studied in shock waves over the temperature range 1800 – 2200 K, monitoring absorption-time profiles at 248 nm. Besides contributions from  $CF_2$ , the signals showed strong absorptions from secondary reaction products, probably mostly  $CH_2F$  formed by the reaction of  $CHF + H_2 \rightarrow CH_2F + H$ . Rate constants of a series of possible secondary reactions were modeled, such as falloff curves for the thermal dissociations of CHF,  $CHF_2$ , and  $CH_2F$  and rate constants of the reactions  $CHF + CH_2F_2 \rightarrow CHF_2 + CH_2F$ ,  $CHF + H_2$  $\rightarrow CH_2F + H$ ,  $H + CH_2F_2 \rightarrow CHF_2 + H_2$ ,  $H + CF_2 \rightarrow CF + HF$ , and  $H + CF \rightarrow C + HF$ . On this basis concentration-time profiles were simulated and compared with experimental absorption-time profiles.

#### References

Cobos, C. J. et. al., *J. Phys. Chem. A* 2017, **121**, 7813 – 7819. Cobos, C. J. et. al., *J. Phys. Chem. A* 2017, **121**, 7820 – 7826.

\*Corresponding author: lars.soelter@chemie.uni-goettingen.de

## Tropospheric Degradation of Biomass Burning Compounds: OH Radical-initiated Oxidation of Three Dimethoxybenzene Isomers and 4-Vinylguaiacol.

Rodrigo G. Gibilisco<sup>a\*</sup>, Ian Barnes<sup>a</sup>, Iustinian Bejan<sup>b</sup> and Peter Wiesen<sup>a</sup>

<sup>a</sup>Bergische Universität Wuppertal, Institute for Atmospheric and Environmental Research, 42097 Wuppertal / Germany

<sup>b</sup>Faculty of Chemistry and CERNESIM Centre, "Al. I. Cuza" University, Iasi, Romania

#### Keywords

biomass burning, dimethoxybenzene, 2-methoxy-4-vinylphenol (4-vinylguaiacol), OH rate coefficients

Biomass burning produces substantial amounts of different -alkyl, -hydroxy, -nitro and methoxy substituted aromatic hydrocarbons, originated mainly by pyrolysis of lignin. (Hatch et al., 2015; Iinuma et al., 2010; Stockwell et al., 2015). Either from primary sources by direct emission from combustion processes or secondary by tropospheric oxidation of emitted precursors, the presence of a diverse and large amount of oxygenated aromatics is expected in the atmosphere, in both, gas and particulate phase.

The present research investigates the rate coefficients for the reactions of OH radicals with the following atmospherically relevant oxygenated aromatic compounds: 1,2 dimethoxybenzene (1,2DMB); 1,3 dimethoxybenzene (1,3DMB); 1,4 dimethoxybenzene (1,4DMB) and 2-methoxy-4-vinylphenol (2MVP). Experiments where performed at 298 K and 1000 mbar of air using a relative rate method in a 1080 L simulation chamber. At least two reference hydrocarbons have been employed for each studied compound. The following rate coefficients (in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) were obtained:  $k_{(OH + 1,2DMB)} = (3.45\pm0.17) \times 10^{-11}$ ,  $k_{(OH + 1,3DMB)} = (4.31\pm0.20) \times 10^{-11}$ ,  $k_{(OH + 1,4DMB)} = (8.85\pm0.40) \times 10^{-11}$ , and  $k_{(OH + 2MVP)} = (1.56\pm0.82) \times 10^{-10}$ . Atmospheric lifetimes have been calculated and possible atmospheric implications assessed.

Acknowledgement:

The authors acknowledge financial support from European grant EUROCHAMP-2020, R. Gibilisco acknowledges the Alexander von Humboldt foundation, I. Bejan acknowledges the UEFISCDI grant PN-III-P4-ID-PCE-2016-0807.

#### References

Hatch, L.E., Luo, W., Pankow, J.F., Yokelson, R.J., Stockwell, C.E., Barsanti, K.C., 2015. Identification and quantification of gaseous organic compounds emitted from biomass burning using two-dimensional gas chromatography-time-of-flight mass spectrometry. Atmos. Chem. Phys. 15, 1865.

Iinuma, Y., Böge, O., Herrmann, H., 2010. Methyl-nitrocatechols: Atmospheric tracer compounds for biomass burning secondary organic aerosols. Environ. Sci. Technol. 44, 8453.

Stockwell, C.E., Veres, P.R., Williams, J., Yokelson, R.J., 2015. Characterization of biomass burning emissions from cooking fires, peat, crop residue, and other fuels with high-resolution proton-transferreaction time-of-flight mass spectrometry. Atmos. Chem. Phys. 15, 845.

## GAS-PHASE DEGRADATION OF 2-BUTANETHIOL INITIATED BY CI ATOMS. KINETICS, PRODUCT YIELDS AND MECHANISM AT 298K AND ATMOSPHERIC PRESSURE

Alejandro L. Cardona<sup>1</sup>, <u>Rodrigo Gibilisco<sup>2</sup></u>, Peter Wiesen<sup>2</sup> and Mariano Teruel<sup>1\*</sup> <sup>1</sup>LUQCA-Instituto de Investigaciones en Fisicoquímica de Córdoba, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba / Argentina. <sup>2</sup> Institute for Atmospheric and Environmental Research, Bergische Universität Wuppertal, 42097 Wuppertal / Germany.

Keywords

2-butanethiol, H-atom abstraction, rate coefficient, product yields, SO<sub>2</sub>.

In the atmosphere, sulfur is key to many environmental issues including acid rain and climate change. Volatile organic sulfur compounds (VOSC) can exist at high concentrations. They are released into the environment from many natural and anthropogenic sources. The presence of 2-butanethiol was detected in the air from sewerage treatment tanks of chemical petroleum, geothermal areas, muddy beach water and wastewater treatment plants (Li and Shooter, 2004; 1985; Sye and Chen, 2000). It reaches the troposphere mainly through organic matter decomposition and is removed by gas phase reactions in the atmosphere e.g. with OH radicals and Cl atoms. The aim of this work was to investigate the kinetics, mechanism and product yields for the reaction of 2-butanethiol with Cl atoms, at atmospheric pressure of synthetic air and at 298K. The experiments were performed in a 480 L chamber of a cylindrical borosilicate glass vessel with 32 fluorescent lamps coupled to a FTIR spectrometer to enables "in situ" monitoring of the reactants in the infrared range 4000-700 cm<sup>-1</sup>. The kinetics was studied using the relative kinetic method and the quantification of reactants and products was performed by comparison with calibrated reference spectra. The rate coefficient obtained by averaging the values from different experiments was  $k_{Cl} = (3.2 \pm 0.7) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , in agreement with previous work for alkyl thiols. In addition, products studies were performed at the same conditions in synthetic air and NO<sub>x</sub> free conditions. The identified products were HCl, 2butanone and SO<sub>2</sub> with the corresponding yields of  $(97\pm2)$  %,  $(38\pm3)$ % and  $(57\pm2)$ %, respectively. A degradation mechanism was proposed for the pathways leading to the formation of the identified products. The observed high yields in the reaction system indicate that the Hatom abstraction at the S-H group is an important pathway for the reaction of Cl atoms with 2butanethiol.

#### References

Li, K.-C., Shooter, D., 2004. Analysis of sulfur-containing compounds in ambient air using solid-phase microextraction and gas chromatography with pulsed flame photometric detection. Int. J. Environ. Anal. Chem. 84, 749–760.

Sye, W., Chen, W., 2000. Determination of odorous sulfur compounds in air by Tenax GR preconcentration and capillary gas chromatography in combination with flameless sulfur chemiluminescence detection. Toxicol. Environ. Chem. 77, 207–218.
## PHOTODEGRADATION OF A SERIES OF FLUOROESTERS INITIATED BY OH RADICALS AT DIFFERENT TEMPERATURES

P. Lugo<sup>1</sup>, C. Rivela<sup>1</sup>, <u>R. Gibilisco<sup>2</sup></u>, S. Salgado<sup>3</sup>, P. Wiesen<sup>2</sup>, M. B. Blanco<sup>1\*</sup> and M. A. Teruel<sup>1</sup>

<sup>1</sup> Instituto de Investigaciones en Fisicoquímica de Córdoba (I.N.F.I.Q.C.), Dpto. de Fisicoquímica. Facultad de Ciencias Químicas, Universidad Nacional de Córdoba. Ciudad Universitaria, 5000 Córdoba, Argentina.

<sup>2</sup> Institute for Atmospheric and Environmental Research, Bergische Universität Wuppertal, 42097 Wuppertal, Germany.

<sup>3</sup> Departamento de Química Física, Facultad de Ciencias Químicas, Universidad de Castilla La Mancha, Avda Camilo José Cela 10, 13071 Ciudad Real, Spain.

Keywords:

2,2,2-Trifluoroethylmethacrylate, 1,1,1,3,3,3-hexafluoroisopropylacrylate, 1,1,1,3,3,3-hexafluoroisopropylmethacrylate, 2,2,2-trifluoroethylacrylate, rate coefficients, tropospheric chemistry

Fluorinated acrylates and methacrylates are unsaturated esters with a wide range of industrial applications, since they are functional monomers used for the development of a new family of  $\frac{1}{2}$ 

fluorine-containing vinyl polymers for Hi-Tech applications.<sup>1</sup> The atmospheric degradation of these unsaturated compounds is initiated mainly by chemical reaction with OH and NO3 radicals and O3 molecules contributing to tropospheric ozone production and the formation of other secondary photo-oxidants in polluted areas.

The aim of this study was to determine rate coefficients of the following reactions:

$CH_2 = C(CH_3)C(O)OCH(CF_3)_2$	+	OH	>	Products,	$k_1$
$CH_2 = C(CH_3)C(O)OCH_2CF_3$	+	OH	>	Products,	$k_2$
CH <sub>2</sub> =CHC(O)OCH <sub>2</sub> CF <sub>3</sub>	+	OH		Products,	<i>k</i> <sub>3</sub>
$CH_2 = CHC(O)OCH(CF_3)_2$	+	OH	>	Products	$k_4$

The experiments were performed in the temperature range 287-313 K and atmospheric pressure of synthetic air using a 1080 L photoreactor coupled with FTIR analysis to monitor the decay of the organic species and the reference compounds. The kinetic data obtained were used to derive the following Arrhenius expressions (in units of cm<sup>3</sup> molecule<sup>-1</sup>s<sup>-1</sup>):  $k_1 = (4.73 \pm 1.09) \times 10^{-13} \exp[(442 \pm 28)/T]$ ,  $k_2 = (1.44 \pm 1.26) \times 10^{-13} \exp[(1504 \pm 69)/T]$ ,  $k_3 = (7.14 \pm 1.34) \times 10^{-13} \exp[(1021\pm 89)/T]$  and  $k_4 = (1.91 \pm 0.69) \times 10^{-17} \exp[(4213 \pm 579)/T]$ .

This is the first temperature dependence study of the four reactions shown above. Negative temperature dependencies of the rate constants were obtained in agreement with an addition to the double bond as the main reaction pathway.

In addition, we have estimated through the kinetic data obtained in this work, the atmospheric lifetimes of the fluorinated compounds at different temperatures and their variations with altitude.

#### References

1. Boschet, F., Kostov, G., Ameduri, B., Yoshida, T., Kosuke, K., 2010. J Phys Org Chem. 2008; 21(5):397-401.

# Towards a common C<sub>0</sub>-C<sub>2</sub> mechanism: a critical evaluation of rate constants for hydrogen combustion kinetics.

M. Pelucchi<sup>1</sup>\*, U. Burke<sup>2</sup>, L. Cai<sup>3</sup>, K. P. Somers<sup>2</sup>, P. Glarborg<sup>4</sup>, T. Turanyi<sup>5</sup>, H. Pitsch<sup>3</sup>, H. J. Curran<sup>2</sup>, T. Faravelli<sup>1</sup>, S. J. Klippenstein<sup>6</sup>

<sup>1</sup>CRECK Modeling Lab - Politecnico di Milano, Milano - ITALY

<sup>2</sup>Combustion Chemistry Centre - National University of Ireland, Galway - IRELAND

<sup>3</sup>Institute for Combustion Technology - RWTH Aachen University, Aachen - GERMANY

<sup>4</sup>Department of Chemical and Biochemical Engineering - Technical University of Denmark,

#### Lyngby - DENMARK

<sup>5</sup>Institute of Chemistry - Eötvös Loránd University (ELTE), Budapest – HUNGARY <sup>6</sup>Chemical Sciences and Engineering Division – Argonne National Laboratory, Argonne – USA

#### Keywords

Hydrogen, Syngas, Kinetics, Core mechanism, Review

Since the pioneering studies of Tsang and Hampson (1986), and of Baulch and co-workers (1992 and 2005), the knowledge of elementary combustion kinetics has increased, largely due to more accurate theory, advanced computing facilities and progress in experimental measurements (Klippenstein, 2017). However, little effort has been devoted to the collection and reinterpretation of this knowledge after the early 2000s. A modern perspective on historical and recent data is long overdue given the significant progresses mentioned above, and the utility of "Baulch-style" reviews.

Starting in February 2017, we have collected and interpreted a very large number of direct and indirect rate constant measurements from the literature, as well as every state of the art theoretical calculation available for 50 elementary reaction steps involved in H2/CO pyrolysis and combustion. The data for each reaction are analyzed, and fitted to a form of utility in kinetic modelling, with appropriate uncertainty bounds assigned. Unlike the Baulch reviews, each experimental rate constant is accompanied by an appropriate ab-initio/TST/Master-Equation analysis to extrapolate over the entire regimes of temperature and pressure of relevance to combustion. In some cases, the coupling of theory with the experimental analyses served the goal of cross-validating both theory and experiments (e.g.  $HO_2+HO_2$ ), while for instances where experimental data are very sparse (e.g.  $O+HO_2=O_2+OH$ ), theory provided a reliable basis to discern between experiments and to determine more accurate kinetic parameters.

This joint effort aims to propose a fundamentally based state of the art mechanism for syngas combustion, with associated uncertainties, to serve as a reference for the entire combustion kinetics community. For different reasons, models for real fuels available in the literature rely on C0-C2 subsets that involve significant differences. These differences often do not have substantial impacts on the overall performances as different rate constants in the core mechanism are often compensated by different rates in the model subset relating to heavier fuels. This leads to similar radical distributions and therefore to similar macroscopic behavior. However, the adoption of a fundamentally based common core mechanism will constitute a substantial thrust to increase the robustness of higher molecular weight fuel's kinetics.

#### References

Tsang W, et al. Journal of Physical and Chemical Reference Data 15.3 (1986): 1087-1279. Baulch DL, et al., Journal of Physical and Chemical Reference Data 21.3 (1992): 411-734. Baulch DL, et al., Journal of Physical and Chemical Reference Data 34.3 (2005): 757-1397.

\*Corresponding author: matteo.pelucchi@polimi.it

## Kinetics and mechanism of BrHgO• reaction with CO

D. Khiri<sup>1</sup>, T. S. Dibble<sup>2</sup>, I. Cernusak<sup>3</sup> and F. Louis<sup>1\*</sup>

<sup>1</sup>Univ. Lille, CNRS, UMR 8522-PC2A, PhysicoChimie des Processus de Combustion et de

l'Atmosphère, 59000 Lille, France

<sup>2</sup>Department of Chemistry, State University of New York-College of Environmental Science and Forestry, 1 Forestry Drive, Syracuse, New York 13210, United States

<sup>3</sup>Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Ilkovičova 6, 84215 Bratislava, Slovakia

Keywords

Atmosphere; mercury; potential energy surface.

Oxidation of Hg(0) to Hg(II) in the gaseous atmosphere largely limits the rate of its transfer to ecosystems. Global oxidation of Hg(0) is largely initiated by atomic bromine. The resulting BrHg radical mostly reacts with NO<sub>2</sub> to make BrHgONO, which, in turn is rapidly photolyzed to BrHgO• (see Scheme 1). Recent work by Lam et al. (2019 a,b) indicates that BrHgO• reacts analogously to OH radical. This led us to investigate whether this analogy extends to reaction with CO:

BrHgO• + CO 
$$\rightarrow$$
 BrHg• + CO<sub>2</sub>  $\Delta H_r^\circ = -280 \text{ kJ/mole}$  (1)

 $HO \bullet + CO \rightarrow H + CO_2 \qquad \Delta H_r^\circ = -98 \text{ kJ/mole}$  (2)

The structures of reactive species have been investigated using MP2 geometries with a small core pseudopotential for Br and Hg together with a triple-zeta basis set for their valence electrons and the aug-cc-pVTZ basis set for C and O. Energies have been evaluated at the CCSD(T)/CBS level of theory including different corrections (ZPE, CV, SR, and SOC).

Like OH + CO, BrHgO• forms a pre-reactive complex with CO. The subsequent reaction of the BrHgO-CO complex to form BrHgOCO proceeds with a much lower barrier than the ~7 kJ mol<sup>-1</sup> barrier for HO-CO  $\rightarrow$  HOCO. The BrHgO-CO bond is as strong as the HO-CO bond (~110 and 130 kJ mol<sup>-1</sup> for the trans and cis isomers, respectively). Dissociation of BrHgOCO to form BrHg• + CO<sub>2</sub> is exothermic by 160-180 kJ mol<sup>-1</sup> and proceeds over barriers of less than 7 kJ mol<sup>-1</sup>. This contrasts the endothermic and high-barrier reaction of HOCO to form H + CO<sub>2</sub>. We expect that reaction (1) possesses a higher rate constant than the reaction (2), but kinetic calculations are still in progress at this time.

#### References

Lam KT, Wilhelmsen CJ, Dibble, TS. BrHgO• +  $C_2H_4$  and BrHgO• + HCHO in Atmospheric Oxidation of Mercury: Determining Rate Constants of Reactions with Pre-Reactive Complexes and a Bifurcation. J Phys Chem A 2019; under revision.

Lam KT, Wilhelmsen CJ, Schwid AC, Jiao Y, Dibble, TS. Computational Study on the Photolysis of BrHgONO and the Reactions of BrHgO• with  $CH_4$ ,  $C_2H_6$ , NO, and NO<sub>2</sub>: Implications for Formation of Hg(II) Compounds in the Atmosphere, J Phys Chem A 2019;123: 1637-1647.

\* florent.louis@univ-lille.fr

## DIRECT MEASUREMENTS OF THE KINETICS OF THE REACTION BETWEEN THE CRIEGEE INTERMEDIATE CH<sub>3</sub>CHOO AND SO<sub>2</sub>

Lavinia Onel<sup>1,\*</sup>, Jennifer Mortiboy<sup>1</sup>, Mark Blitz<sup>1,2</sup>, Paul Seakins<sup>1,2</sup>, Dwayne Heard<sup>1,2</sup> and Daniel Stone<sup>1</sup>

<sup>1</sup>School of Chemistry, University of Leeds, LS2 9JT Leeds, UK <sup>2</sup>National Centre for Atmospheric Science (NCAS), University of Leeds, LS2 9JT Leeds, UK

Keywords

CH<sub>3</sub>CHOO, syn and anti conformers, kinetics, SO<sub>2</sub>, flash photolysis, broadband UV, absorption spectroscopy.

Criegee intermediates are formed by the ozonolysis of unsaturated volatile organic compounds emitted from both biogenic and anthropogenic sources. CH<sub>3</sub>CHOO Criegee intermediate exists as two conformers, *syn*, where CH<sub>3</sub> group is in the proximity of the terminal O atom, and *anti*. Previous studies have shown rapid gas phase reactions of the CH<sub>3</sub>CHOO conformers with SO<sub>2</sub> at low pressures (Howes et al., 2018; Sheps et al., 2014; Taatjes et al., 2013). The reaction is expected to generate SO<sub>3</sub>, which then leads to the production of H<sub>2</sub>SO<sub>4</sub>(g) and sulphate aerosols in the troposphere. We have carried out direct measurements of the kinetics of *syn-* and *anti*-CH<sub>3</sub>CHOO with SO<sub>2</sub> at 296 K as a function of pressure using flash photolysis of CH<sub>3</sub>CHI<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> mixtures at 248 nm with time-resolved multipass broadband UV absorption spectroscopy. In the absence of SO<sub>2</sub>, the reaction of the *anti*-conformer with the CH<sub>3</sub>CHI<sub>2</sub> precursor dominates the removal of *anti*-CH<sub>3</sub>CHOO under laboratory conditions. The reaction of the *syn-*conformer with CH<sub>3</sub>CHI<sub>2</sub> is ~10 times slower. We will also report the yield of CH<sub>3</sub>CHOO following photolysis of CH<sub>3</sub>CHI<sub>2</sub> and the ratios of *syn:anti* conformers.

#### References

Howes NUM, Mir ZS, Blitz MA, Hardman S, Lewis TR, Stone D, Seakins PW. Kinetic studies of C1 and C2 Criegee intermediates with SO<sub>2</sub> using laser flash photolysis coupled with photoionization mass spectrometry and time resolved UV absorption spectroscopy. PCCP 2018; 20: 22218-22227.

Sheps L, Scully AM, Au K. UV absorption probing of the conformer-dependent reactivity of a Criegee intermediate CH<sub>3</sub>CHOO. PCCP 2014; 16: 26701-26706.

Taatjes CA, Welz O, Eskola AJ, Savee JD, Scheer AM, Shallcross DE, Rotavera B, Lee EPF, Dyke JM, Mok DK, Osborn DL, Percival CJ. Direct measurements of conformer-dependent reactivity of the Criegee intermediate CH<sub>3</sub>CHOO. Science 2013; 340: 177-180.

Vereecken L, Harder H, Novelli A. The reaction of Criegee intermediates with NO, RO<sub>2</sub>, and SO<sub>2</sub>, and their fate in the atmosphere. PCCP 2012; 14: 14682-14695.

## Gas-Phase Positive Ion Insights during Laboratory EUV Irradiation of N<sub>2</sub>/CH<sub>4</sub> Gas Mixtures: Implications for Titan's Ionospheric Chemistry

Jérémy Bourgalais<sup>1</sup>, Nathalie Carrasco<sup>1</sup> and Pascal Pernot<sup>2</sup>

<sup>1</sup>Université Versailles St-Quentin, Sorbonne Université, UPMC Univ. Paris 06, CNRS/INSU, LATMOS-IPSL, 11 boulevard d'Alembert, 78280 Guyancourt, France

<sup>2</sup>Laboratoire de Chimie Physique, CNRS, Univ. Paris-Sud, Université Paris-Saclay, 91405, Orsay, France

Keywords

Planetary Atmosphere – Photochemistry – Mass Spectrometry – Plasma Discharge

The arrival of the *Cassini-Huygens* spacecraft led to the discovery of an unexpected efficient organic chemistry, including very heavy ionic species in the Titan's thermosphere. It showed that large condensable molecules are formed in the upper region of the moon where the solar flux of photons initiates chemical reactions through photoionization and photodissociation of the main species. However, the complexity of the chemistry is far from being understood. Indeed, current photochemical models reasonably explain the formation of small C/N-bearing molecules, but fail at reproducing the abundance of heavy species shedding light on a missing chemistry. It is mainly due to the complexity of reaction pathways and the limited set of available data (*e.g.*, branching ratios, coefficient rates) for chemical reactions.

In order, to refine our knowledge of photochemical processes in Titan's upper atmosphere we present a series of laboratory EUV irradiation experiments. We irradiated at 73.6nm using a UV lamp (Tigrine et al. 2016) different gas mixtures ( $N_2/CH_4$  & He/CH<sub>4</sub>) in a photochemical reactor. The photoproducts were monitored *in situ* using a quadrupole mass spectrometer. Then, characterization of the species was achieved by confronting experimental observations and numerical predictions from a 0D-photochemical model used to reproduce the chemistry in the cell. (Peng et al. 2014) Monte Carlo based sensitivity analysis allowed us to identify the key formation and loss reactions.

Our conjugated approach coupling numerical simulation with experimental measurements shed light on the key role played by small N-bearing molecules as intermediates towards the formation of complex nitrogenized organic molecules. In this work we bring for the first time information about both ionic species formed in Titan's ionospheric simulation experiments and highlight the most important molecules and the key chemical pathways in Titan's upper atmosphere.

#### References

Tigrine, S., Carrasco, N., Vettier, L., et al. (2016). J. Phys. D: App. Phys., 49(39), 395202. Peng, Z., Carrasco, N., & Pernot, P. (2014). GeoResJ, 1, 33.

## Gas phase kinetic study for a series of methylated furans with chlorine atoms in atmospheric conditions

Claudiu Roman<sup>1,2</sup>, Cecilia Arsene<sup>1,2</sup>, Romeo-Iulian Olariu<sup>1,2</sup>, and Iustinian Gabriel Bejan<sup>1,2\*</sup>

<sup>1</sup>Department of Chemistry, "Alexandru Ioan Cuza" University of Iasi, Romania <sup>2</sup>Integrated Center of Environmental Science Studies in the North Eastern Region - CERNESIM, "Alexandru Ioan Cuza" University of Iasi, 11 Carol I, 700506 Iasi, Romania

#### Keywords

alkylated furans, gas phase kinetic, chlorine atoms

Furans are emitted into the atmosphere mainly from anthropogenic activities and in a less extent from biogenic sources. Due to their high reactivity against the main atmospheric oxidants, they are potential precursors for ozone generation and secondary organic aerosol (SOA) formation (Calvert et al., 2011).

As part of a systematic study performed at CERNESIM laboratories in Iasi, Romania, to determine the reactivity of alkylated furans towards relevant atmospheric oxidizing species, these investigations report the gas phase reaction rate coefficients in air at  $298\pm2K$  and  $1000\pm2$  mbar for the chlorine atoms initiated reactions with a series of methylated furans. Furan (FN), 2-methylfuran (2-MF), 3-methylfuran (3MF), 2,3-dimethylfuran (2,3DMF), 2,5-dimethylfuran (2,5DMF) and 2,3,5-trimethylfuran (2,3,5TMF) were investigated in 760L ESC-Q-UAIC quartz glass photoreactor using long path Fourier Transform Infrared Spectroscopy (FTIR). Chlorine atoms were generated in situ by the photolysis of oxalyl chloride at 254 nm. Rate coefficients for the reaction of these compounds with OH radicals were determined using the relative kinetic technique, with acrolein, *E*-2-butene and isoprene as reference compounds.

For the investigated (alkylated)-furans, significant agreement was observed with the existing literature rate coefficient values (Cabanas et al., 2005) and with those estimated values obtained by using the Structure Activity Relationship (SAR) approach. Investigations performed in this study have determined the rate coefficient for a series of furans starting with  $k_{\text{FN+CL}}=1.87\times10^{-10}$  cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup> with increasing reactivity trends for alkylated furans with the number of methyl groups added on the ring.

These kinetic studies represent first reported rate coefficient values for reaction of 2,3DMF and 2,3,5TMF with Cl atoms. The kinetic results will be presented together with an assessment of the atmospheric importance of chemical degradation of furans.

Acknowledgements: The financial support provided by UEFISCDI within the PN-III-P4-ID-PCE-2016-0807 (IGAC-CYCLO) PN-III-P4-ID-PCE-2016-0270 (OLFA-ROA) projects is gratefully acknowledged. European Union's Horizon 2020 research and innovation programme through the EUROCHAMP-2020 Infrastructure Activity under grant agreement No. 730997 is also gratefully acknowledged

#### References

Calvert, J. G., et al., The mechanisms of atmospheric oxidation of the oxygenates, Oxford University Press, New York (2011).

Cabañas, B., et al., Study of reaction processes of furan and some furan derivatives initiated by Cl atoms, Atmos. Environ., 2005; 39(10):1935-1944.

\*Corresponding author: iustinian.bejan@uaic.ro

## UNIMOLECULAR DECOMPOSITION OF THE ALLYLIC METHYL CROTONATE RADICAL: EXPERIMENTAL AND MODELLING STUDY

Prasenjit Seal, Satya P Joshi and Arkke J Eskola<sup>\*</sup> Department of Chemistry, University of Helsinki, P. O. Box 55 (A. I. Virtasen aukio 1), Helsinki 00014, FINLAND

#### Keywords

Allylic methyl crotonate radical, unimolecular decomposition, gas-phase kinetics, photoionization mass-spectrometer, master equation modelling.

In the present work, the unimolecular decomposition of the allylic radical. •CH<sub>2</sub>CHCHC(O)OMe (Zhou et al., 2018) obtained from the 248 nm photolysis of methyl 5methyl-2-hexenoate (i-PrCH<sub>2</sub>CHCHC(O)OMe) was investigated both from experimental and theoretical points of view. The unimolecular decomposition was measured using a tubular laminar flow reactor coupled with a photoionization mass-spectrometer (PIMS). Pulsed excimer laser photolysis of the precursor molecule was used to produce radical of interest homogeneously along the reactor. Direct, time-resolved experiments of the radical decays were performed at low pressures (0.5–9 Torr) over the temperature range 750–869 K using He and N<sub>2</sub> carrier gases. The measured unimolecular rate coefficients were found to be close to highpressure limit under the experimental conditions. We also performed ab initio quantum chemistry calculations to generate the potential energy surface of the unimolecular reaction using the domain-based local pair natural orbital (DLPNO) coupled cluster methods along with density functional theory. The unimolecular rate coefficients were then estimated from the master equation modelling and compared with the experimental findings.

#### References

Zhou X, Zhai Y, Ye L, Zhang L. Theoretical studies on the reaction kinetics of methyl crotonate with hydroxyl radical. Sustainable Energy Fuels 2018;2:392-402.

## Kinetics of the gas phase reaction between the Criegee intermediate CH<sub>2</sub>OO and O<sub>3</sub>

Lavinia Onel<sup>1,\*</sup>, Mark Blitz<sup>1,2</sup>, Paul Seakins<sup>1,2</sup>, Dwayne Heard<sup>1,2</sup> and Daniel Stone<sup>1</sup>

<sup>1</sup>School of Chemistry, University of Leeds, LS2 9JT Leeds, UK <sup>2</sup>National Centre for Atmospheric Science (NCAS), University of Leeds, LS2 9JT Leeds, UK

Keywords

Criegee intermediate, kinetics, ozone, flash photolysis, time-resolved, broadband UV, absorption spectroscopy.

A significant fraction of unsaturated volatile organic compounds are oxidised by O<sub>3</sub>, producing highly reactive Criegee intermediates, such as the simplest Criegee, CH<sub>2</sub>OO, in the atmosphere. The reaction of stabilised CH<sub>2</sub>OO with O<sub>3</sub> has received relatively little attention, and there are large uncertainties in the value of its rate coefficient at 298 K: the only previous experimental study (Chang et al., 2018) determined  $(6.7 \pm 0.5) \times 10^{-14}$  cm<sup>3</sup> s<sup>-1</sup> and there are significant discrepancies between theoretical studies (~  $10^{-18} - 4 \times 10^{-13}$  cm<sup>3</sup> s<sup>-1</sup>) (Kjaergaard et al., 2013 and Vereecken et al., 2015). We have performed a kinetic study of the reaction at 296 K and 300 Torr using a novel flash photolysis experiment coupled with time-resolved multipass broadband UV absorption spectroscopy. CH<sub>2</sub>OO has been generated by photolysing CH<sub>2</sub>I<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> mixtures at 248 nm. The broadband UV absorption experiments permit reagent concentrations which avoid aerosol formation in the system on the time scale of the kinetic measurements. The simultaneously numerical fit of thirty CH<sub>2</sub>OO temporal decays gives a rate coefficient of (3.6 ± 0.8) × 10<sup>-13</sup> cm<sup>3</sup> s<sup>-1</sup>, which is in agreement with the theoretical value of 4 × 10<sup>-13</sup> cm<sup>3</sup> s<sup>-1</sup> reported by Vereecken et al. (2015).

#### References

Chang Y.P., Chang H.H. and Lin J.M. Kinetics of the simplest Criegee intermediate reaction with ozone studied using mid-infrared quantum cascade laser spectrometer. PCCP 2018; 20: 97-102.

Kjaergaard H.G., Kurtén T., Nielsen L.B., Jørgensen S. and Wennberg P.O. Criegee Intermediates React with Ozone. J Phys Chem Lett 2013; 4: 2525–2529.

Vereecken L., Rickard A.R., Newlandde M.J. and Bloss W.J. Theoretical study of the reactions of Criegee intermediates with ozone, alkylhydroperoxides, and carbon monoxide. 2015; 17: 23847-23858.

## A new kinetics database of organic oxidation reactions for use in structure-activity relationship studies

M.R. McGillen<sup>1,2,\*</sup> J.J. Orlando<sup>3</sup>, A. Mellouki<sup>1</sup>, B. Picquet-Varrault<sup>4</sup>, T.J. Wallington<sup>5</sup>, W.P.L. Carter<sup>6</sup>

<sup>1</sup>CNRS-INSIS, Institut de Combustion, Aérothermique, Réactivité et Environnement 1C, Avenue de la recherche scientifique, 45071 Orléans cedex 2, France

<sup>2</sup>Le Studium Loire Valley Institute for Advanced Studies, Orléans, France

<sup>3</sup>Atmospheric Chemistry Observations and Modeling Laboratory, National Center for Atmospheric Research, Boulder, CO, 80307, USA

<sup>4</sup>Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR 7583 CNRS, Universités Paris-Est Créteil et Paris Diderot, Institut Pierre-Simon Laplace, Créteil Cedex, France

<sup>5</sup>Research & Advanced Engineering, Ford Motor Company, Dearborn, MI, 48121-2053, USA

<sup>6</sup>College of Engineering, Center for Environmental Research and Technology (CE-CERT), University of California, Riverside,CA, 92521, USA

Keywords

Structure-activity relationships, Hydroxyl, Chlorine, Ozone, Nitrate.

It is becoming increasingly apparent that structure-activity relationships (SARs) are necessary for understanding systems of real atmospheric complexity, and other complex reaction systems. However, before an SAR can be established, a dataset is required that is reliable and extensive enough that it can be trained on a broad range of representative compounds. The aim of this work is to construct a new database that is thoroughly vetted, searchable and downloadable in full for the reactions of volatile organic compounds with OH, Cl, NO<sub>3</sub> and O<sub>3</sub>. A secondary aim is to recommend only one rate coefficient for a given reaction together with an estimate of its uncertainty. For this purpose, we make use of existing reviews and compendia for many of the reactions of interest, however, it is found that these resources can be of limited scope, and are in need of updating in many cases. We therefore surveyed and included as much additional published kinetic data as possible.

The new database contains kinetic information for ~1700 compounds, with temperature-dependent parameters available for ~800 reactions. It is the largest reviewed compilation of oxidation rate coefficients known to these authors, and allows us to begin to assess the state-of-the-knowledge for gas-phase reactivity in atmospheric science. Although this database is already extensive, it is intended that it can be maintained and upgraded in the future.

It is expected that this database will be of interest to developers of SARs and chemical modellers who require copious kinetic information. It will likewise be of interest to experimentalists who wish to know if a reaction has been studied previously and if so, to compare their results with what is available in the literature.

\*Corresponding author: e-mail address

#### Biological Cmposition of Castal Arborne Prticulate Mtters during

### Enteromorpha Prolifera Outbreak

Jiahui Rong , Song Yu, Yan Wu\*

School of Environmental Science and Engineering, Shandong University,

No.72 Binhai Road, 266237 Qingdao, China

Key words: Enteromorpha Prolifera Outbreak, Microbial Communities, Resistance Genes

Abstract: The effects of Enteromorpha Prolifera Outbreak on coastal airborne particles were investigated in the paper. Air samples were collected using HighBioTrap sampler operated at its standard flow rate of 1000 L/min at different distances (0m, 500m, 1000m) from the seacoast before, during and after the Enteromorpha Prolifera Outbreak. Offshore seawater samples from the same period were also collected. Microbial communities, antibiotic and heavy metal resistance genes, allergens, endotoxins as well as marine algae toxins were analyzed for both air and seawater samples. Results showed that the fungal concentration and diversities in the coastal air were significantly higher during the Enteromorpha Prolifera Outbreak than other two phases. In contrast, which were opposite to bacterial ones. The bacterial DNA concentrations and diversities in the coastal airborne particulates showed an onward trend, while the fungi showed a downward trend. Compared with seawater without Enteromorpha Prolifera, there were more antibiotic and heavy metal resistance genes in atmospheric particles during the outbreak of Enteromorpha Prolifera. And Tansposase *tnpA* and vancomycin resistance genes (*vanB* and *vanRA*) were only detected for air samples collected during the Enteromorpha Prolifera Outbreak. The results from this study provide further new information in biological composition of coastal airborne particulate matters during Enteromorpha Prolifera Outbreak.

#### References

Wilson, T.W., Ladino, L.A., et al. A marine biogenic source of atmospheric ice-nucleating particles. Nature, 2015, 525(7568), 234-238.

Cheng, Y.S., Zhou, Y., et al. Characterization of marine aerosol for assessment of human exposure to brevetoxins. Environmental Health Perspectives, 2005,13, 638-643.

## ANTIBIOTIC RESISTANCE GENES IN THE COASTAL AIRBORNE PARTICLES

Song Yu, Jiahui Rong and Yan Wu<sup>\*</sup>

School of Environmental Science and Engineering, Shandong University, No.72

Binhai Road, 266237 Qingdao, China

Keywords

Antibiotic resistance genes; Microbial communities; Air quality conditions; Particle size distributions

This paper is aimed to obtain a detailed list of antibiotic resistance genes in the coastal air with different pollution levels. Air samples were collected by large-flow bioaerosol samplers at different air pollution levels (Good, Moderate, Unhealthy for Sensitive Groups, Unhealthy, Very Unhealthy, and Hazardous). At the same time, the particle size distributions were monitored by TSI particle counters. Air samples were analyzed using Illumina Miseq sequencing for the microbial community structure, and qPCR for the antibiotic resistance genes. The results showed that the increase of air pollution level increased the abundance of antibiotic resistance genes. The *blaCTX-M* in  $\beta$ -lactams and the *ermF* in macrolides are the most abundant antibiotic resistance genes. The abundant antibiotic resistance genes in the coastal atmosphere may rise the number of resistant bacteria in the atmosphere and transfer the resistance determinants to other pathogenic bacteria, posing a potential threat to human health. This work aimed to provide new information of antibiotic resistance genes in coastal air with different pollution levels, and further clarify the possible impacts on human health under different air quality conditions.

#### References

Matyar F, Akkan T, Ucak Y. Aeromonas and Pseudomonas: antibiotic and heavy metal resistance species from Iskenderun Bay, Turkey (northeast Mediterranean Sea) 2010; 167:309-320.

Ma L, Li A, Yin X, et al. The Prevalence of Integrons as the carrier of antibiotic resistance genes in natyral and man-made environments. Environmental Science and Technology 2017; 51:5721-5728.

Xie JW, Jin L, Luo XS, Zhao Z, Li XD. Seasonal Disparities in Airborne Bacteria and Associated Antibiotic Resistance Genes in PM 2.5 between Urban and Rural Sites. Environmental Science and Technology 2018; 5: 74-79.

## Preliminary results on tracing air pollution and impact on ozone in different plumes using aircraft measurements in DACCIWA European project

Chaoyang Xue<sup>1</sup>, Gisèle Krysztofiak<sup>1\*</sup>, Vanessa Brocchi<sup>1</sup>, Greta Stratmann<sup>2</sup>, Daniel Sauer<sup>2</sup>, Hans Schlager<sup>2</sup>, James Lee<sup>3,4</sup>, James Hopkins<sup>3</sup>, Aurélie Colomb<sup>5</sup>, Agnès Borbon<sup>5</sup> and Valéry Catoire<sup>1</sup>

<sup>1</sup> Laboratoire de Physique et Chimie de l'Environnement et de l'Espace (LPC2E), CNRS – Université Orléans – CNES, 45071 Orléans cedex 2, France.

<sup>2</sup> Institut für Physik der Atmosphäre, Deutsches Zentrum für Luft und Raumfahrt, Oberpfaffenhofen, Germany.

<sup>3</sup> National Centre for Atmospheric Science, University of York, York, UK

<sup>4</sup> Wolfson Atmospheric Chemistry Laboratories, University of York, York, UK

<sup>5</sup> Laboratoire de Météorologie Physique, Université Clermont Auvergne, Clermont-Ferrand, France

Keywords

Pollution emissions, aircraft measurements, ozone production, trajectories modelisation

Within the framework of the European DACCIWA project (Dynamics-aerosol-chemistry-cloud interactions in West Africa), several aircraft measurements have been conducted in July 2016 to study emissions from oil rigs, maritime traffic, industrial area, cities or biomass burning in the Gulf of Guinea. Several instruments have been used on-board the DLR Falcon-20, Safire ATR-42 and the BAS Twin-Otter providing measurements of pollutants (NO<sub>2</sub>, NO, CO, O<sub>3</sub>, VOCs, HCHO, aerosols) and meteorological parameters. This is the first measurements of this type <del>are</del> performed in this region, which is yet in great population and economic development. The growth of the oil industry and maritime traffic and, therefore their emissions, along the Guinea Coast contributes to the increase of anthropogenic emission sources. Questions as for the interactions between those anthropogenic sources and natural emissions remain in particular in the ozone formation. Thus, this set of trace gases can be used to fingerprint different sources of local air pollution.

Emissions of individual sources can be quantified by combining the measurements with a nestedgrid regional scale Lagrangian particle dispersion model (FLEXPART, *Stohl et al., 2005*). This study provides preliminary results highlighting the impact of industrial emissions, maritime traffic emissions and oil and gas extraction facilities on the regional air quality.

Comparison of observed  $O_3$  concentration with that predicted by Leighton relationship can be performed to explore the influence of pollutants in the plume on  $O_3$ . In addition, a 0-D box model MCM v3.1 displayed on AtChem online v1.5 (*Bloss et al., 2005*) can be used to explain the variation of OH and HO<sub>2</sub> radicals in the polluted plume and non-pollutedair. Both of the analyses can provide further insight on the chemistry in the plume.

#### References

Stohl, A., Forster C., Frank A., Seibert P., and Wotawa G. (2005): Technical Note: The Lagrangian particle dispersion model FLEXPART version 6.2. Atmos. Chem. Phys., 5, 2461-2474.
Bloss, C., V. Wagner, M.E. Jenkin, R. Volkamer, W.J. Bloss, J.D. Lee, D.E. Heard, K. Wirtz, M. Martin-Reviejo, G. Rea, J.C. Wenger and M.J. Pilling (2005): Development of a detailed chemical mechanism (MCMv3.1) for the atmospheric oxidation of aromatic hydrocarbons. Atmos Chem. Phys., 5, 641-664.

# Examination of automatic generation algorithm of catalyst surface reaction mechanism

Masato Aratani<sup>1</sup> and Teppei Ogura<sup>1,\*</sup> <sup>1</sup>Kwansei Gakuin University, 2-1 Gakuen Sanda Hyogo, 669-1337 JAPAN

#### Keywords

Automatic generation algorithm, catalyst surface reaction mechanism

With the development of computers in recent years, computational analysis by reaction simulators incorporating thermodynamic and kinetic models is increasing. However, since many current simulators manually input elementary reactions, it is necessary to manually change elementary reactions every time the reaction system is changed. This is a complexity task and can be a source of errors. In recent years, development of a program for automatically generating reaction mechanisms that automates these has also been carried out<sup>1,2</sup>. However, these programs are mainly targeted for gas phase reactions in which elementary rate constant data are sufficient, and cannot be directly applied to surface reactions. Therefore, we aimed at the creation of the automatic generation program of the reaction mechanism for the catalyst surface reaction, and examined the algorithm first.

The chemical reaction simulator was improved based on the program written by MATLAB. As an outline of the reaction simulator, the governing equations in the CSTR including the surface reaction are solved at each time step. In order to generate the governing equation automatically for any reactant, the following three step algorithm was considered. Chemical species information required for automatic generation, automatic generation of possible reactions from any chemical species, and estimation of various reaction parameters. Chemical species information was expressed by defining the following seven parameters for each atom in the chemical species, Atomic number, Element, Number of unpaired electrons, Pairs of electrons, Charge, Bonding atom, and Number of bonds. These parameters are necessary for the determination of the elements within the species and the structure of the species. For example, the number of unpaired electrons is important in distinguishing structural isomers such as CHO and COH and describing bonds. Elementary reactions were generated based on chemical species information. The reaction focuses on the number of unpaired electrons and the type of bond, and generates once all possible reactions due to bond dissociation and bonding with other chemical species. After that, using flow analysis, the reaction mechanism is prevented from expanding by discarding the non-main reaction path. In order to automatically generate reaction rate constants, we focused on the estimation of activation energy, enthalpy and entropy, which are the detailed parameters. Since the reaction on the metal surface has a correlation with the d-band gravity center of the surface metal and the work function, etc., it is calculated using an inference equation in consideration of them.

#### References

1) Akira Miyoshi. KUCRS - Detailed Kinetic Mechanism Generator for Versatile Fuel Components and Mixtures. Proc of COMODIA 2012:116-121

2) Connie W.Gao, Joshua W.Allen, William H.Green, Richard H.West. Reaction Mechanism Generator: Automatic construction of chemical kinetic mechanisms. Comput Phys Commun 2016:203:212-225.

## **Reaction Generalization of Singular Site using Local Surface Model**

Yasumasa Takata<sup>1</sup>, Teppei Ogura<sup>1</sup>

<sup>1</sup>School of Science and Technology Kwansei Gakuin University, 2-1Gakuen Sanda City, Hyogo,

JAPAN

#### Keywords

quantum chemical calculation, special site, generalization, hydrocarbon

In order to optimize and improve the catalyst performance suitable for each reaction, it is necessary to understand the reaction mechanism at the active point of the catalyst surface reaction. However, for metal surfaces in high temperature regions, reaction analysis in a single plane orientation is insufficient because the mobility of catalytic metal atoms on the surface increases and the metal atoms move on the surface. It is difficult to observe changes in reactivity due to this surface structure by experiments, and it is necessary to approach from reaction simulation in various surface structures. However, this requires reaction simulation on every surface structures, which is very computationally expensive. Therefore, if the dependence of surface reactions in catalytic reactions on catalyst materials can be classified and generalized, it will be easier to create and analyze detailed surface reaction mechanisms even in unknown catalyst systems. In this study, based on the data of adsorption energy of hydrocarbon chemical species based for methane steam reforming using the local surface model of Ni previously calculated in our laboratory (Liu et al., 2018) we try to generalize the correlation of the adsorption energy at the Ni surface specific site. The generalization of adsorption energy takes into consideration the dependence of the catalyst surface structure in addition to the interaction between the catalyst surface and the adsorbed species. It is known that the adsorption energy depends on the d-band center of the catalyst metal and the work function difference between the catalyst metal surface and the adsorbed species (Shen et al., 2017). Moreover, the valence number of atoms of the

adsorbed species in contact with the catalyst surface has a great influence on the adsorption strength of the adsorbed species (Vallejo et al.,2015). In addition, generalization coordination number (GCN) (Zhao et al.,2016) is used to express surface structure and adsorption site. That is, it was thought that the adsorption energy could be described by a polynomial with d-band center, work function, valence number of adsorbed species and GCN as parameters. Based on these, the polynomial fitting of the adsorption energy on the Ni surface was examined by polynomial fitting the data of the above adsorption energy. Figure 1 shows a comparison of DFT calculations and generalized equations.



#### References

Liu Shixue, Kotani Yosuke, Ogura Teppei Theoretical Study of the Local Structure Effect on Methane Reforming Reaction TOCAT8, Yokohama, 2018, P2165

Vallejo CV, Loffreda David, Koper MTM and Sautet Philippe Nat. Chem. 2015:7:403-410

Zhao Zhonglong, Chen Zhengzheng, Zhang Xu, and Lu Gang. Nat. Chem. 2016:120:28125-28130

Shen Xiaochen, Pan Yanbo, Liu Bin, Yang Jinlong, Zeng Jie and Peng Zhenmeng Phys. Chem. Chem. Phys. 2017;19;12628-12632

\*Corresponding author: e-mail address

## KINETIC ANALYSIS OF GROWTH MECHANISM OF PAHS THROUGH C5 RINGS

Warumporn Pejpichestakul<sup>1</sup>, Matteo Pelucchi<sup>1</sup>, Carlo Cavallotti<sup>1</sup>, Alessio Frassoldati<sup>1</sup>, Tiziano Faravelli<sup>1</sup>

<sup>1</sup>CRECK Modeling Lab, Department of Chemistry Materials and Chemical Engineering, Politecnico di Milano, Piazza Leonardo da Vinci 33, 20133, Milan, ITALY

Keywords

Aromatics, Kinetics, Polycyclic Aromatic Hydrocarbon, Five-Membered Ring

Polycyclic aromatic hydrocarbons (PAHs) are carcinogenic compounds and known precursors forming of carbonaceous particles such as soot. Accurate predictions of soot formations strongly rely on accurate predictions of PAHs chemistry. Most PAH growth pathways depend on the kinetics of  $C_2$ - $C_4$  species. Moreover,  $C_5$  species can also play an important role in the growth process that produce PAH and, eventually, soot. Five-member ring hydrocarbons are key intermediates in cycloalkane combustion giving high amount of resonantly-stabilized cyclopentadienyl radicals that can undergo self-recombination. Several routes converting cyclopentadienyl to aromatic species have been proposed, however, there are still uncertainties in the pathways and associated kinetic parameters.

This work addresses the detailed kinetic modeling of PAH formation aiming at comparing the model predictions with experimental data on pyrolysis of five-membered ring species, i.e. cyclopentene and cyclopentadiene. Specifically, the detailed mechanism is validated against experimental studies under pyrolysis conditions of cyclopentene in a jet-stirred reactor (Herbinet *et al.*, 2016), cyclopentadiene (Butler and Glassman, 2009; Kim *et al.*, 2010; Djokic *et al.*, 2014), as well as, ethylene doped cyclopentadiene (Vervust *et al.*, 2018) in a flow reactor. The validation highlights the critical role of cyclopentadienyl radical in molecular weight growth kinetics leading to the formation of aromatic species. Particular attention is placed on the paths leading conversion of  $C_5$  species to toluene, which was first proposed by a few years ago (Fascella *et al.*, 2005; Cavallotti *et al.*, 2007).

#### References

Butler RG, Glassman I. Proc Combust Inst 2009;32(1):395–402.

Cavallotti C, Mancarella S, Rota R, Carrà S. Conversion of C5 into C6 cyclic species through the formation of C7 intermediates. J Phys Chem A 2007;111(19):3959–3969.

Djokic MR, Van Geem KM, Cavallotti C, Frassoldati A, Ranzi E, Marin GB. Combust Flame 2014;161(11):2739–2751.

Fascella S, Cavallotti C, Rota R, Carrà S. J Phys Chem A 2005;109(33):7546–7557.

Herbinet O, Rodriguez A, Husson B, Battin-Leclerc F, Wang Z, Cheng Z, Qi F. J Phys Chem A 2016;120(5):668–682.

Kim DH, Mulholland JA, Wang D, Violi A. J Phys Chem A 2010;114(47):12411–12416.

Vervust AJ, Djokic MR, Merchant SS, Carstensen HH, Long AE, Marin GB, Green WH, Van Geem KM. Energy Fuels (2018);32(3):3920–3934.

## IUPAC TASK GROUP ON ATMOSPHERIC CHEMICAL KINETIC DATA EVALUATION

M. Ammann<sup>1</sup>, R.A. Cox<sup>2</sup>, J.N. Crowley<sup>3</sup>, H. Herrmann<sup>4</sup>, M.E. Jenkin<sup>5</sup>, V.F. McNeill<sup>6</sup>, A. Mellouki<sup>7</sup>, J. Troe<sup>8</sup>, and T.J. Wallington<sup>9</sup>

 (1) Laboratory of Environmental Chemistry, Paul Scherrer Institut, CH-5232 Villigen, Switzerland
 (2) Centre for Atmospheric Science, Dept. of Chemistry, University of Cambridge, Lensfield Road Cambridge CB2 1EP, UK

(3) Max-Planck-Institut für Chemie, Division of Atmospheric Chemistry, Mainz, Germany

(4) Leibniz-Institut für Troposphärenforschung (TROPOS), 04318 Leipzig, Germany

(5) Atmospheric Chemistry Services, Okehampton, Devon EX20 1FB, UK

(6) Department of Chemical Engineering, Columbia University, New York, NY 10027, USA

(7) ICARE, CNRS Orleans, France

(8) Institute of Physical Chemistry, University of Goettingen, Tammannstr. 6, D-37077 Goettingen, Germany

(9) Ford Motor Company, Research and Advanced Engineering, Mail Drop RIC-2122, Dearborn, Michigan 48121-2053, USA

Emissions from human activities have led to important changes in the composition of the atmosphere. Computational models are used to understand the impacts of emissions on air quality on local, regional, and global scales and the global climate system. An accurate representation of atmospheric chemistry is of critical importance in these models. The mission of the IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation is to provide evaluated kinetic data for gas-phase, heterogeneous, and aqueous-phase reactions. The data are published periodically in a special issue of Atmospheric Chemistry and Physics here http://www.atmos-chem-phys.net/special\_issue8.html

## GAS PHASE KINETIC STUDY FOR A SERIES OF METHYLATED AROMATICS WITH OH RADICALS

Iustinian Gabriel Bejan<sup>1\*</sup>, Rodrigo G. Gibilisco<sup>2</sup>, Ian Barnes<sup>2</sup> and Peter Wiesen<sup>2</sup>

<sup>1</sup>Department of Chemistry and Integrated Center of Environmental Science Studies in the North Eastern Region - CERNESIM, "Alexandru Ioan Cuza" University of Iasi, Romania
<sup>2</sup>Bergische Universität Wuppertal, Institute for Atmospheric and Environmental Research, 42097 Wuppertal / Germany

#### Keywords

methylated aromatics, gas phase kinetic, OH radicals

Aromatic hydrocarbons (AHs) are emitted in the urban atmosphere from human activities. AHs contribute significantly to the formation of atmospheric photooxidants (30% of total) and are responsible up to 10% of global secondary organic aerosol (SOA) formation with anthropogenic contribution. These compounds are also associated with human health problems. The OH radical initiated oxidation of benzene, toluene, xylenes and trimethylbenzenes were intensively studied (Calvert et al., 2002) but the highly methylated benzenes received less attention.

The aim of this study was to determine rate coefficients for the reaction of highly methylated benzenes with OH radicals to assess the relative importance of these reactions as atmospheric loss processes. The kinetics of the reactions of OH radicals with 1,2,4,5-tetramethylbenzene (1245TMB), pentamethylbenzene (PMB) and hexamethylbenzene (HMB) have been investigated at 298±2K and atmospheric pressure of air using a relative rate method. The experiments were performed in a 1080 l volume quartz glass photo-reactor (QUAREC) using in situ FTIR analysis to monitor the decay of the methylated benzenes and the reference compounds. The reference compounds employed in these investigations were propene and isoprene. The following rate coefficients (in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) were obtained:

k(1245TMB+OH)	$=(5.36\pm0.89)\times10^{-11}$
<i>k</i> (PMB+OH)	$= (9.14 \pm 1.53) \times 10^{-11}$
<i>k</i> (HMB+OH)	$=(1.23\pm0.34)\times10^{-10}$

The rate coefficient value determined in this study is in perfect agreement with those found in literature for 1245TMB. The rate coefficients for PMB and HMB obtained in this work are slightly smaller in comparison with Alarcon et al., (2015) study which have used FP-RF technique in their investigations. However, the values are in reasonable agreement considering the range of calculated errors. The kinetic data will be discussed in terms of reactivity trends. From these investigations several interesting reactivity patterns have emerged and these will be discussed based on the current understanding of aromatic hydrocarbon oxidation.

Acknowledgements: The financial support provided by UEFISCDI within the PN-III-P4-ID-PCE-2016-0807 (IGAC-CYCLO) is gratefully acknowledged. EUROCHAMP-2020 grant agreement 730997 is also acknowledged.

#### References

Alarcon, P., Bohn, B., and Zetzsch, C., *Phys.Chem.Chem.Phys.*, 2015, 17, 13053. Calvert, J. G., et al., The mechanisms of atmospheric oxidation of the aromatic hydrocarbons, Oxford University Press, New York (2002).

## **EFFECTS OF THE AXIAL LIGANDS ON THE FORMATION KINETICS OF WATER-SOLUBLE CERIUM(III) PORPHYRINS**

Zsolt Valicsek<sup>\*</sup>, Melitta Patrícia Kiss and Ottó Horváth Department of General and Inorganic Chemistry, Institute of Chemistry, Faculty of Engineering, University of Pannonia, P.O.B. 158, H-8201 Veszprém, Hungary

#### Keywords

out-of-plane metalloporphyrins; lanthanide(III) ions; cerium; insertion kinetics; axial enhancement and hindrance.

The kinetics of the insertion of cerium(III) ion into the coordination cavity of the widely used, anionic, 5,10,15,20-tetrakis(4-sulfonatophenyl) porphyrin was investigated in both the absence and the presence of various potential axial ligands in water: acetate as bidentate anionic, chloride as monodentate anionic, ethylene glycol as bidentate neutral, and ethanol as monodentate neutral axial ligands. The hindering, blocking effects of axial ligands, regarding the formation of bisporphyrin complexes are well-known in the literature. However, their potential effects on the formation of lanthanide(III) monoporphyrin complexes were not studied in deep details. The bidentate O-donor acetate ligands have stronger effects on the insertion of cerium(III) into the cavity of the anionic porphyrin than the monodentate and softer chloride ions do; originating rather from steric, than electronic aspects. However, the neutral axial ligands (ethanol and ethylene glycol), as bridges, result in a special aggregation between cerium(III) and the porphyrin cavity. Our results indicate that the association of the axially ligated cerium(III) and the anionic porphyrin is not the only rate-determining step in the mechanism of complex formation.

This work was supported by the Széchenyi 2020 under the GINOP-2.3.2-15-2016-00016.

#### References

Imran M, Kiss MP, Valicsek Z, Horváth O. Formation, photophysics and photochemistry of anionic lanthanide(III) mono- and bisporphyrins. Molecules 2019;24:1309-1322.

Horváth O, Valicsek Z, Fodor MA, Major MM, Imran M, Grampp G, Wankmüller A. Visible light-driven photophysics and photochemistry of water-soluble metalloporphyrins. Coord. Chem. Rev. 2016;325:59–66.

### Chamber study of the Oxalyl Chloride Photodissociation in Sunlight

A. Kukui<sup>1</sup>, Y. Ren<sup>2</sup>, Valéry Catoire<sup>1</sup>, V. Daele<sup>2</sup>, A. Mellouki<sup>2</sup>, and A.R. Ravishankara<sup>2,3,4</sup>

<sup>1</sup>LPC2E-CNRS, Laboratoire de Physique et de Chimie de l'Environnement et de l'Espace, Orléans, France

<sup>2</sup> ICARE-CNRS, Institut de Combustion, Aérothermique, Réactivité et Environnement, Orléans, France

<sup>3</sup> Departments of Chemistry and Atmospheric Science, Colorado State University, Fort Collins,

USA

<sup>4</sup> Le Studium Loire Valley Institute for Advanced Studies, Orléans, France

Keywords

Photolysis, Oxalyl Chloride, Chamber, Kinetics, Peroxy Radicals, CIMS

Oxalyl chloride,  $(ClCO)_2$ , is commonly used as a photolytic Cl atoms precursor for kinetic and photochemical studies. Previous studies of the  $(ClCO)_2$  photodissociation at 193, 248, and 351 nm suggest that UV photodissociation proceeds via a two-step mechanism involving the formation of an excited ClCO\* radical (1) and dissociation of a fraction of the ClCO\* depending on the photolysis wavelength to Cl + CO (2):

 $(ClCO)_2 + hv \rightarrow ClCO^* + CO + Cl \quad (1)$ ClCO\*  $\rightarrow$  Cl + CO (2)

The ClCO radical formed with the energy lower than its dissociation barrier has been found to undergo thermal unimolecular dissociation (3) on the time scale of several microseconds at room temperature and atmospheric pressure:

 $ClCO + M \rightarrow Cl + CO + M$  (3)

In this work the photodissociation of  $(COCl)_2$  by solar irradiation has been studied in the HELIOS environmental chamber. An effective  $(COCl)_2$  dissociation quantum yield of  $0.34\pm0.03$  has been derived from the measured actinic flux in the chamber and the observed  $(COCl)_2$  decay rate. This result is to be expected based on previous studies. The relative yields of CO and Cl atoms were derived by comparing the  $(COCl)_2$  loss rate with the production rates of CO and Cl atoms. The Cl production rate was derived from the measured by CIMS steady state HO<sub>2</sub> or CH<sub>3</sub>O<sub>2</sub> radical concentrations generated by scavenging of Cl by H<sub>2</sub> or CH<sub>4</sub>, respectively. The obtained relative CO yield of  $2.2\pm0.1$  per  $(ClCO)_2$  loss is in agreement with previous studies. The relative yield of Cl has been found to be 2 times lower,  $1.01\pm0.03$  per  $(ClCO)_2$  loss, in disagreement with previous studies and suggesting potentially another mechanism of the  $(COCl)_2$  photodissociation at wavelengths longer than 300 nm.

\*Corresponding author: alexandre.kukui@cnrs-orleans.fr

## LAMINAR BURNING VELOCITY OF BIOGAS AND SYNGAS FLAMES

Toufik Boushaki<sup>1,2,\*</sup>, Hajar Zaidaoui<sup>1</sup>, Pascale Gillon<sup>1</sup>, Brahim Sarh<sup>1,2</sup> <sup>1</sup>ICARE CNRS, 1C Avenue de la Recherche Scientifique, 45071 Orléans, FRANCE <sup>2</sup>Université d'Orléans, 6 Avenue du Parc Floral, 45100 Orléans, FRANCE

Keywords

Laminar burning velocity, Biogas flame, Syngas flame, Combustion.

The energy needs are in continuous growth which depends highly on fossil fuels. For this reason, renewable energies appear as a sustainable tool to complement and partially replace fossil fuels in energy production. Biomass, one of the autonomous sectors of renewable energy, is characterized by its neutrality in  $CO_2$  emissions during its life cycle and by a low content of nitrogen and sulfur which results in low emissions of NOx and SO<sub>2</sub>. In this work we are interested in studying the combustion of gases issued from anaerobic digestion (mainly  $CH_4$ - $CO_2$ ) and gasification (H<sub>2</sub>-CO). Numerical calculations of laminar burning velocity, flame temperature and pollutant emissions are performed using the COSILAB code for 1D premixed flame. Note that the laminar burning velocity is an important parameter for validating chemical kinetics, for the modeling of turbulent combustion and for the design of practical devices. Effects of different parameters as temperature and pressure of fresh gases, equivalence ratio and gas composition on flame characteristics are analyzed. Several mechanisms of chemical reactions as GRI-Mech3.0, GRI Skeletal, San Diego mechanism, NIU GALWAY, CRECK Modeling Group, S. Davis et al. mechanism are used and compared to the results from the literature. Results show that calculations with some these mechanisms reproduce well experimental results of the literature. Results of biogas flames show that CO<sub>2</sub> addition induces a decrease in laminar burning velocity, an increase in CO emissions and a decrease in NOx formation. Calculations of syngas flames show that the hydrogen increase leads to an increase of laminar burning velocity and flame temperature. This is due to the higher reactivity and higher flammability limits with hydrogen addition.



Figure 1. Laminar burning velocities of biogas and syngas flames versus equivalence ratio.

\*Corresponding author: toufik.boushaki@cnrs-orleans.fr

## INCOHERENT BROAD-BAND CAVITY ENHANCED ABSORPTION SPECTROSCOPY FOR SENSITIVE AND RAPID MOLECULAR IODINE DETECTION IN THE PRESENCE OF AEROSOLS AND WATER VAPOUR

Chiheb Bahrini<sup>1,2\*</sup>, Anne-Cécile Grégoire<sup>1</sup>, Dorel Obada<sup>1</sup>, Christian Mun<sup>1</sup> and Christa Fittschen<sup>3</sup> <sup>1</sup>Institut de Radioprotection et de Sûreté Nucléaire (IRSN), Cadarache, 13115 Saint Paul lez Durance, FRANCE

<sup>2</sup> Institut préparatoire aux études d'ingénieurs de Tunis, 2 Rue Jawaher Lel Nehru 1089 Montfleury, TUNISIE

<sup>3</sup> Université Lille 1, CNRS, UMR 8522 – PC2A – Physicochimie des Processus de combustion et de l'atmosphère, 59000 Lille, FRANCE

#### Keywords

Optical metrology; Sensors; Optical resonators; Absorption Spectroscopy; Instrumentation; Light-emitting diodes (LEDs); Optical extinction; Molecular iodine; aerosol.

The atmospheric chemistry of iodine is important in different environments, and particularly in case of a nuclear reactor severe accident. This paper describes the performance of an Incoherent Broad-Band Cavity Enhanced Absorption Spectroscopy (IBB-CEAS) device, based on a green LED source allowing the online detection of gaseous molecular iodine. Light of around 530 nm excites several rovibronic lines of the  $B \leftarrow X$  electronic transition of  $I_2$ . High sensitivities and a wide dynamic range are obtained. The performances and limitations of the IBB-CEAS technique for measurements of iodine in the presence of aerosols and water vapour are discussed.

The performances achieved are illustrated by high sensitivity recordings of the very weak absorption spectrum of water vapour in the wavelength region accessible by our LED.

The capabilities of this device to perform kinetics studies on iodine have been investigated in the framework of nuclear reactor accident research. The re-vaporization process of deposited CsI by optical monitoring of  $I_2$  concentration-time profiles is presented.

#### References

Johansson O, Mutelle H, Parker A E, Batut S, Demaux P, Schoemaecker C, Fittschen C, Appl. Phys. B 2014;114: 421-432.

Saiz-Lopez A, Saunders R W, Joseph D M, Ashworth S H, Plane J M C, Atmos. Chem. Phys. 2004. 4: 1443-1450.

Fiedler S E, Hese A, Ruth A A, Chem. Phys. Lett. 2003; 371: 284-294.

Bahrini C, Grégoire A -C, Dorel O, Mun C and Fittschen C, Opt. Laser Technol. 2018; 108: 466-479.

## Author Index

Østerstrøm Freja Akio Fuwa Al Ajami Mohamad Albaladejo José Albaladejo, José Alturaifi Sulaiman Ammann M. Angelaki Maria Antiñolo María Aranda María Inmaculada Aratani Masato Archer-Nicholls Scott Archibald Alexander T. Arsene Cecilia Asensio María Bahrini Chiheb Ballesteros, Bernabé Balucani Nadia Barnes Ian Barone Vincenzo Battin-Leclerc Frédérique Battin-Lelcerc Frédérique **Batut Sébastien** Batut Sébastien Bayon, Alicia Bedjanian Yuri **Bejan** Iustinian Belhadj Nesrine **Benoit Roland** Berasategui Matias **Bierkandt Thomas Bissember** Alex Blázquez Sergio Blanco M. B. Blitz Mark **Blondal Katrin** Bolshova Tatiana Bolshova Tatyana Borbon Agnès Bose Arnab Bourgalais Jérémy Boushaki Toufik Brackmann Christian Brennan Alexander

Brezinsky Kenneth Briceno John Brocchi Vanessa Brown Steven S. Bry Alain Burke Ultan Buttgen René Cabañas Beatriz Cai Liming Calimet Bénédicte Canosa, André Cantrel Laurent Cao Chuang-Chuang Capriolo Gianluca Carabineiro Hugo Caracciolo Adriana Carbonnier Maxime Carrasco Nathalie Carter William Carvalho Teresa Casavecchia Piergiorgio Caster Kacee Catoire Valéry Catorie Laurent Cavallotti Carlo Cernusak Ivan Chao Wen Chatterjee Debabrata Chaumeix Nabiha Chen Jianmin Chesnokov Evgeni Chhantyal-Pun Rabi Chu Te-Chun Ciampi Simone Cirtog Manuela Claudiu Roman Cobos Carlos **Coddeville Patrice** Colomb Aurélie Comandini Andrea **Constales** Denis Cooke Ellie Cooper Sean Cox R. Crowley J.

Crowley John Cummins Katherine Cuoci Alberto Curran Henry

Döntgen Malte Daële Véronique **Dagaut Philippe** Daily John Damien Amedro Dao Duy Quang Dayma Guillaume De Andrade Claudia De Joannon Mara De Persis Stephanie **Delannoy Romain** Dibble Theodore **Dievart Pascal Ding Yiming Dmitriev** Artm Dominik Krüger Donne, Scott **Durif Olivier** Dusanter Sébastien Edtbauer Achim El Bakali Abderrahman Ellison G. Barney Elothmani Hajar Eskola Arkke

Fan Hanyu Faravelli Tiziano Farooq Aamir Fedunik-Hofman, Larissa Fernandes Yann Ferracci Valerio Fikri Mustapha Fittschen Christa Flaud Pierre-Marie Forsuelo Michael Foucher Fabrice Fouqueau Axel Fournet Rene Frassoldati Alessio Fuller Mark

Galabov Boris García-Sáez Alberto Garcia Gustavo Gasnot Laurent Gaudion Vincent Geiser Markus George Christian Gerasimov Ilya Gibilisco Rodrigo Giri Binod **Glarborg** Peter Glaude Pierre-Alexandre Godinho Tiago Goldsmith C. Franklin **Goldsmith Franklin** Golka Leonie Gomez Saulo Gonchikzhapov Munko González Daniel Gonzalez Joaquin Goulay Fabien Goussougli Matieyendou Grabow Lars Grajales Gonzalez Edwing Grambow Colin Gratzfeld Dennis Green William Green William H. Gromotka Zoë Guermouche Saliha Guillaume Dayma Guzman Juan

Höner Martin Haack Alexander Han Lei Hanson Ronald Heard Dwayne Hemberger Patrick Herbinet Olivier Herrmann Hartmut Herrmann J. Herzler Juergen Heufer Karl Hopkins James Horváth Ottó Horvath Raphael Huang Can Hugi Andreas

Idir Mahmoud Iyer Siddharth Izumi Naoto

Jelic Jelena Jenkin M. Jiménez Elena Jimenez Martinez, Elena Jocher Agnes Joshi Satya

Köhler Markus Kühn Christian Kéromnès Alan Kaczmarek Dennis Kajii Yoshizumi Kanno Nozomu Karakaya Yasin Kasper Tina Khaled Fethi Khan Anwar Khanniche Sarah Khiri Dorra **Kiss Melitta** Kito Tomohiro Knyazkov Denis Kol De Carvalho Rita Konnov Alexander Korobeinichev Oleg Koshlyakov Pavel Kounlavong Sommy Krasnoperov Lev Kravtchenko Florent Krysztofiak Gisèle Kukkadapu Goutham Kukui Alexandre Kunioshi Nilson Kurten Theo

L. Cardona Alejandro Labbe Nicole Laich Andrew Lailliau Maxence Le Moyne Luis Le Picard Sébastien Lee James Lee Yoon Lefort Benoîte

Lemos Francisco Lemos Maria Amélia Leonardis Thierry Li Wei Li Xiao Li Yuyang Lin Jim Jr-Min Lipinski, Wojciech Liu Mengjie Liu Yue-Xi Liu Zhong-Kai Locoge Nadine Louis Florent Lu Yu Lubrano Lavadera Marco Lugo P. Lupi Jacopo

Ma Siyuan Manna Maria Marin Guv Martín Pilar Martin Rebecca Masaya Tadini Wenyika Mathieu Olivier Mazeau Emily McGill Charles McGillen Max McNeill V. Faye Mei Bowen Mellouki Abdelwahid Mermet Kenneth Methling Torsten Mokrani Nabil Molina Angela Moliner Vicent Monge Palacios Manuel Morozov Igor Mortiboy Jennifer Mughees Ali Syed Mulvihill Clayton Munko Gonchikzhapov

Nahon Laurent Namysl Sylvain Neupane Sneha Nguyen Thanh Nguyen Thanh Binh Nicholls Thomas Ninnemann Erik Noda Kaito

Oguchi Tatsuo Ogura Teppei Olariu Romeo Olzmann Matthias Onel Lavinia Orlando John Orr-Ewing Andrew Osborn David Osipova Ksenia Osseiran Noureddin

Panaget Thomas Papadimitriou Vassileios Pappijn Cato Parr Joseph Pejpichestakul Warumporn Pekkanen Timo Pelucchi Matteo Pereira Patrícia Pernot Pascal Perraudin Emilie Petersen Eric Peukert Sebastian Picquet-Varrault Bénédicte Pillier Laure Pimenta Amilcar Pitsch Heinz Portefield Jessica Pratali Maffei Luna

#### Qi Fei

Raghu Amrutha Ragucci Raffaele Ranzi Eliseo Ravishankara A R Ravishankara A.r. (ravi) Ravishankara Akkihebbal Rayez Jean-Claude Rayez Marie-Thérèse Ren Yangang Rey Francisca Reyniers Marie-Françoise Ribaucour Marc Richaud Emmanuel Rijo Bruna Rissanen Matti Rivella C. Robertson Johnathon Rogers Cory **Romanias Manolis** Rong Jiahui S Varunkumar Sölter Lars Sabia Pino Sakai Yasuyuki Salgado S. Salgado Sagrario Salin Alexey Salta Zoi Sangwan Manuvesh Sarathy Subram Sasaki Yu Sauer Daniel Saufi Abd Sauvage Stéphane Schaefer Thomas Schlager Hans Schoemaecker Coralie Schulz Christof Seakins Paul Seal Prasenjit Segovia Marc Sela Paul Serinyel Zeynep Shallcross Dudley Shannon Robin Shmakov Andrey Sirjean Baptiste Smith Mica Somers Kieran Stanton John Stephen Klippenstein Stone Daniel Strand Christopher Stratmann Greta Studt Felix Suliman Siba

Taamali Sonia Taamalli Sonia Takahashi Kaito Takata Yasumasa Tarelho Luís Tasinato Nicola Tellbach Elsa Teruel Mariano Thevenet Frederic Thurmond Kyle Tian Zhen-Yu Timonen Raimo Tognetti Vincent Tomas Alexandre Tovar Carmen Tran Luc-Sy Troe J. Troe Jürgen Troe Juergen Turanyi Tamas Uwagwu Awele

Valicsek Zsolt Van De Vijver Ruben Van Geem Kevin Vanhove Guillaume Vasu Subith Ventura Oscar Vermeire Florence Villenave Eric Vogel Yan

Wakamatsu Katsuhiro Wallington T. Wallington Timothy Wang Guoqing Wang Jiaxing Wang Zhandong Weber Isabelle West Richard Westbrook Charles Westmoreland Phillip Whalley Lisa Wiesen Peter Williams Jonathan Wu Xiaoqing Wu Yan Xue Chaoyang

Yablonsky Gregory Yan Chao Yang Bin Yang Jeehyun Yang Jiu-Zhong Yoshihiro Jagawa Yu S Yu Song Yuan Wenhao

Zádor Judit Zachhuber Nicholas Zaidaoui Hajar Zetzsch Cornelius Zhai Yi-Tong Zhang Feng Zhang Jia Zhang Xiaokai Zhang Xiaoyuan Zhang Yan Zhou Chong-Wen Zhou Li Zhou Zijun Zhukov Victor