



**25th International
Symposium on Gas Kinetics
& Related Phenomena**

22nd - 26th July 2018

Lille, France

Royal Society of Chemistry Gas Kinetics Committee

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Anne Burlet-Parendel

Opening, Chair: Andrew Rickard

9h00 Introduction

9h20 Plenary Lecture: A. Ravishankara, Colorado State University **p. 17**
Association Reactions: My Associations with Prof. Ian W.M. Smith

10h00 Olivier Durif, Institut de Physique de Rennes
CRESUSOL, a New Instrument for Determining Kinetics and Branching Ratios of Elementary Processes at low Temperatures

10h20 David Bones, University of Leeds
Field Observations, Laboratory Measurements and Model Simulations of Ni Ablation and Subsequent Chemical Reactions in the Earth's Mesosphere.

10h40 Coffee break

Atmospheric Chemistry I, Chair: Stanley Sander

11h20 Plenary Lecture: Geoffrey Tyndall, NCAR Boulder **p. 20**
Formation of Alkyl Nitrates from Some Mid-Sized Alkanes

12h00 Damien Amedro, MPI Mainz
Re-evaluation of the Rate Constant for OH + NO₂ – The Effect of H₂O on one of the Most Important Atmospheric Reactions

12h20 Lei Zhu, Wadsworth Center, New York State University
Role of 2-Nitrophenol and Methyl-2-nitrophenol Photolysis as Missing Sources of OH and HONO in Some Polluted Environments: Implications from Laboratory Studies

12h40 Presentation of RSC Environment Medal to Dwayne Heard, University of Leeds

12h50 Lunch

New Methods, Chair: Aamir Farooq

- 14h10 Plenary Lecture: Sebastien Dusanter, IMT Lille Douai **p. 23**
Integrated Measurements of Atmospheric Chemistry: Moving Laboratory Experiments into the Field
- 14h50 Graham Boustead, University of Leeds
Development of a Photo-fragmentation Laser Induced Fluorescence Instrument for the Measurement of Nitrous Acid
- 15h10 Aileen Hui, California Institute of Technology
Direct Detection of OH Radicals using mid-IR 2-f Frequency Modulation Spectroscopy for Temperature Dependence Studies of $\text{HO}_2 + \text{CH}_3\text{C}(\text{O})\text{O}_2$
- 15h30 Frank Winiberg, Jet Propulsion Laboratory
Study of key OH + NO_x/NO_z reactions under upper troposphere/lower stratosphere conditions
- 15h50 Coffee break and photo on the stairs in the entrance hall

Combustion I, Chair: Gernot Friedrichs

- 16h30 Plenary Lecture: Frédérique Battin-Leclerc, CNRS Nancy **p. 27**
Recent Progress on Hydroperoxide Chemistry during Gas-phase Oxidation of Fuel Components
- 17h10 Zachary Buras, Sandia National Laboratories
Using OH and HO₂ Radicals as Markers of Biofuel Ignition Properties
- 17h30 Fethi Khaled, King Abdullah University of Science and Technology
On the Reaction Kinetics of Dienes with OH Radicals
- 17h50 One-minute flash presentation of posters presented by PhD students

- 18h10 Odd numbers Poster session, beer and food** **p. 76**
All around the plenary hall

Structure-Activity Relationship, Chair: Mark Blitz

- 9h00 Plenary Lecture: Tim Wallington, Ford Motor Company **p. 31**
Structure Activity Relationships for Atmospheric Models: Current Status and Future Outlook
- 9h40 Mark Goldman, Massachusetts Institute of Technology
Fate of Peroxy Radicals in Atmosphere, Combustion, and Everywhere in Between
- 10h00 Max McGillen, University of Bristol
An Assessment of Structure-Activity Relationship Performance in Predicting the Gas-Phase Rate Coefficients of Organic Compounds with Hydroxyl, Ozone, Nitrate and Chlorine
- 10h20 Luc Vereecken, Forschungszentrum Jülich
Validation and Extension of a Structure-Activity Relationship for Reactions of Criegee Intermediates
- 10h40 Coffee break

Atmospheric Chemistry II, Chair: John Orlando

- 11h20 Jim Lin, Academia Sinica, Taipei **p. 35**
Kinetics of Criegee Intermediates
- 10h40 Mohamad Al Ajami, University of Lille
ROOOH: the Missing Piece of the Puzzle for OH measurements in low NO Environments
- 12h00 Diego Medeiros, University of Leeds
Investigations of OH Recycling in the Isoprene + OH Reaction in the Presence of Oxygen: Shedding Light on the Missing OH
- 12h20 Barbara Nozière, CNRS Lyon
Speciated Monitoring of Organic Peroxy Radicals: First Laboratory Applications
- 12h40 Lunch

Astrochemistry, Chair: Sébastien Le Picard

- 14h10 Plenary Lecture: Catherine Walsh, University of Leeds **p. 39**
Astrochemistry: Molecule Formation at the Frontier of Physics
- 14h50 Elena Jimenez, University of Castilla – La Mancha
Ultra-low Temperature Kinetics of the OH-Reaction with Oxygenates in the Interstellar Medium
- 15h10 Niclas West, University of Leeds
Low Temperature Gas Phase Reaction Rate Coefficient Measurements: Toward Modeling of Stellar Winds
- 15h30 Xiaofeng Tang, Chinese Academy of Sciences
Multiplex Synchrotron VUV Photoionization Methods for Radical Reactions in Atmospheric Chemistry: $\text{CH}_3 + \text{O}_2$
- 15h50 Coffee break

Combustion II, Chair: Nathalie Lamoureux

- 16h30 Te-Chun Chu, Massachusetts Institute of Technology **p. 43**
Phenyl Radical Addition to Unsaturated Hydrocarbons: Product Distributions & Rates
- 16h50 Kacee Caster, West Virginia University
Investigations into the Reaction of Cyclopentadiene with CH Radicals: A Novel Route to Benzene Formation
- 17h10 Cato Pappjin, Ghent University
Thermal Decomposition of Sulfur Compounds: Kinetic Modeling and Experimental Validation
- 17h30 James Thorpe, University of Florida
Modeling the Thermal Decomposition of Methyl Acetate: a Study in Combustion
- 17h50 One-minute flash presentation of posters presented by PhD students
- 18h10 Even numbers Poster session, beer and food**
All around the plenary hall

Multiphase Chemistry, Chair: Khatuna Kakhiani

- 9h00 Plenary Lecture: Barbara d'Anna, CNRS Marseille **p. 48**
SOA Formation from Photooxidation of Vehicle Exhaust Emissions
- 9h40 Fabien Goulay, West Virginia University
Effect of Dimerization on the OH-Initiated Heterogeneous Oxidation of Saccharide Nanoparticles
- 10h00 Chia Wang, National Sun Yat-sen University, Taiwan
Probing the Electronic Structures, Interfacial Solvation Properties and Surface pH of Organic-containing Aqueous Nanoaerosols
- 10h20 Césaire Fotsing Kwetche, University of Lille
Combining Quantum Chemistry with Classical Molecular Dynamics for the Theoretical Study of Radical Reactivity at the Surface of Organic Aerosols
- 10h40 Matti Rissanen, University of Helsinki and Zhandong Wang, King Abdullah University of Science and Technology
Highly Oxidized Products from Rapid Alkane Autoxidation Part 1 – Implications for Atmospheric Secondary Organic Aerosol Formation
Highly Oxidized Products from Rapid Alkane Autoxidation Part 2 – Implications for Ignition in Combustion Science
- 11h10 Coffee break

Combustion III, Chair: Zeynep Serinyel

- 11h50 Franklin Goldsmith, Brown University **p. 54**
Decomposition Kinetics for HONO and HNO₂
- 12h10 Ruben Van de Vijver, Sandia National Laboratories
KinBot: Automated Stationary Point Localization on Potential Energy Surfaces
- 12h30 Ghanshyam Vaghihani, Air Force Research Lab
High-level Multi-reference Wave Function and Density Functional Theory
Treatment of the N₂H₃ + NO₂ Reaction
- 12h50 Lunch bag and departure for excursion

Elementary processes, Chair: Scott Kable

- 9h00 Plenary Lecture, Matt Costen, Heriot-Watt University **p. 58**
Inelastic and Reactive Scattering at Gas-Liquid Interfaces
- 9h40 Jeremy Bougalais, Université de Versailles Saint Quentin en Yvelines
Gas-Phase Radical Reactions with Hydrocarbons and Amines Probed by Multiplexed
Synchrotron VUV Photoionization Mass Spectrometry
- 10h00 Mitchio Okumura, California Institute of Technology
Kinetic Isotope Effect in the Reactions of OH and O(¹D) with Isotopologues of
Methane
- 10h20 Adriana Caracciolo, Università degli Studi di Perugia
Crossed Molecular Beams and Theoretical Studies of the O(³P) + 1,2-Butadiene
Reaction: Primary Products, Branching Ratios and Intersystem Crossing
- 10h40 Coffee break

Atmospheric Chemistry III, Chair: Jean-François Doussin

- 11h20 Plenary Lecture: Andreas Hofzumahaus, Forschungszentrum Jülich **p. 64**
Atmospheric Simulation Chamber Experiments: Bridging the Gap Between
Laboratory and Field Studies
- 12h00 Gabriel Da Silva, University of Melbourne
Isomerization and Decomposition of Isoprene's Delta-(Z)-Hydroxyperoxyl Radicals
- 12h20 Rasmus Otkjær, University of Copenhagen
Atmospheric Autoxidation is Increasingly Important in Urban and Suburban North
America
- 12h40 Lunch

Chamber Studies, Chair: Alexandre Tomas

- 14h10 Peter Wiesen, University of Wuppertal p. 65
A Gas Kineticist's Life: a Reminiscence to Dr. Ian Barnes
- 14h30 Mike Newland, University of York
The Photolysis Mechanism of Monoaromatic Ring Opening Products - Unsaturated 1,4 Dicarboxyls - from Chamber Experiments
- 14h50 Iustinian Gabriel Bejan, University "Al. I. Cuza" Iasi
Products and Mechanisms for the Atmospheric Oxidation of Dimethylbenzoquinones
- 15h10 Axel Fouqueau, LISA, University of Paris Est - Créteil
Reactivity of γ -Terpinene and α -Terpinene with NO_3 Radical: a Comparative Kinetic and Mechanistic Study
- 15h30 Freja F. Oesterstroem, University of Leeds
Kinetic Study of the $\text{CH}_3\text{O}_2 + \text{HO}_2$ Cross-reaction in the Highly Instrumented Reactor for Atmospheric Chemistry
- 15h50 Coffee break

Combustion IV, Chair: Jürgen Troe

- 16h30 Rajakumar Balla, Indian Institute of Technology, Madras p. 70
Cl Atom Initiated Photo-oxidation Reaction Kinetics of Methyl and Ethyl Propionate
- 16h50 Isabelle Weber, Karlsruher Institut für Technology
Thermal Decomposition of CH_3I Revisited: Consistent Calibration of I-atom Concentrations Behind Shock Waves with Dual I-/H-ARAS
- 17h10 Michael Burke, Columbia University
Pressure Dependence of Chemically Termolecular Reactions
- 17h30 Polanyi lecture: Barbara Finlayson-Pitts p. 74**
University of California Irvine

Multiphase Chemistry in the Atmosphere: It All Starts with Gases

- 19h30 Banquet at the Omnia Restaurant

Odd numbers (in white) will be presented on **Monday**

Even numbers (in grey) will be presented on **Tuesday**

Poster with **yellow** or **blue** names participate in best student poster prize on **Monday** and **Tuesday**

No	Presenter's name	Title
1	Mohammed ALABBAD	Reaction Kinetics for the Unimolecular Decomposition of C ₅ and C ₆ Cyclic Ketones
2	Mark BLITZ	Determination of the HOOCH ₂ OCH ₂ (QOOH) + O ₂ rate coefficient under propagating / branching conditions
3	Joseph BOZZELLI	Computational Study of α -Acrolein Radical Association Reactions with 3O ₂ , Thermochemistry and Kinetics s
4	Adriana CARACCILO	Crossed beam studies of the O(³ P) reaction dynamics with benzene and toluene: primary products and branching ratios
5	Harish CHAKRAVARTY	Theoretical investigation of the kinetics of low-temperature combustion chemistry of propylbenzene
6	Guillaume DAYMA	Experimental and numerical kinetic study of the oxidation of C ₅ H ₁₀ O ₂ esters isomers
7	Hong Quan DO	Experimental study of atmospheric laminar premixed CH ₄ /O ₂ /N ₂ and CH ₄ /H ₂ /O ₂ /N ₂ flames in sooting conditions
8	Ravi FERNANDES	On the auto-ignition kinetics of ammonia at low temperatures and high pressures
9	Fethi KHALED	A high temperature experimental investigation of allyl self-reaction and allyl + OH
10	Olivier HERBINET	Formation study of NO ₂ and NO in methane oxidation in flow tube at high temperature (up to 1973 K)
11	Corina JANZER	NO ₂ formation in the combustion of n-heptane: Kinetic modeling and comparison to engine measurements with diesel fuel
12	Satya JOSHI	An experimental kinetic study for the reaction between vinyl radicals associated propene molecule and molecular oxygen.
13	Saravanan KUZHANTHAIVELAN	Computational investigations on the thermochemistry and kinetics for the autoignition of 2-pentanone
14	Sonia LARA GOMEZ	Development of a methodology for the chemical characterization of soluble organic fraction (SOF) of the particles generated from (bio)fuels combustion using GC-MS/MS
15	Benoite LEFORT	A comparative high-pressure shock tube study on the ignition of pentanol isomers: 1-, 2- and 3- pentanol
16	Lorena MARRODAN	Jet-stirred low-temperature oxidation of n-pentane: the effect of NO _x addition
17	Lorena MARRODAN	Evaluation of DME as a possible fuel additive through the study of the high-pressure oxidation of its mixtures with acetylene

18	Sylvain NAMYSL	Experimental investigation of butanoic and pentanoic acid oxidation
19	Iliyana NAYDENOVA	Kinetic characteristics related to particulate matter formation in biomass combustion
20	Matthias OLZMANN	The complexity of ignition phenomena in diethyl ether/air mixtures
21	David POTTER	Laser photolysis kinetic studies of methyl tert-butyl ether with OH at low temperatures relevant to combustion
22	Zeynep SERINYEL	A comparative high-pressure jet-stirred reactor study on the oxidation of pentanol isomers: 1-, 2- and 3- pentanol
23	Samantha SIME	Kinetic Studies of tert-Butanol under Low Temperature Combustion Conditions
24	Mica SMITH	Acetylene addition to vinyl and aryl radicals: Experimental investigation of HACA and PAH formation pathways
25	Yu SONG	The sensitizing effects of NO ₂ and NO on methane low temperature oxidation in a jet stirred reactor
26	Elsa TELLBACH	Experimental and Modelling Study of the Multichannel Thermal Dissociations of CH ₃ F and CH ₂ F
28	Luc-Sy TRAN	High-pressure low-temperature oxidation of diethyl ether compared to n-pentane and their mixture
29	Florence VERMEIRE	The oxidation of furfural in a jet-stirred reactor: a combined experimental and modeling approach
30	Charlotte WHELAN	Kinetics of OH radical reactions with 2,5-dimethylfuran
32	Emmanuel ASSAF	Rate Constants of the Reactions of DO ₂ + DO ₂ and HO ₂ + DO ₂
33	Simone Thirstrup ANDERSEN	Atmospheric Chemistry of n-CH ₃ (CH ₂) _x CN (x = 0-4) and n-CH ₂ =CH(CH ₂) _x CN (x = 0-4): Kinetics and Mechanisms
34	Josep M. ANGLADA	Atmospheric oxidation of CH ₃ OOH and CH ₃ OOOH by OH
35	Beatriz CABAÑAS	Kinetic study of saturated alcohols during day-time: Reactivity of 3,3-dimethyl-1-butanol and 3,3-dimethyl-2-butanol
36	William CARTER	Structure-Reactivity Evaluation Panel for Gas-Phase Atmospheric Reactions of Organic Compounds
37	Manuela CIRTOG	Reactivity of NO ₃ radical with ramified unsaturated aldehydes: theoretical approach for kinetic and mechanistic studies
38	Theodore DIBBLE	BrHgO•: Predicting the chemistry of a previously-unknown intermediate in atmospheric mercury oxidation
39	Theodore DIBBLE	OH Radical Can Initiate Oxidation of Hg(0) in the Upper Troposphere
40	Terry DILLON	Rate coefficients for OH + VOC reactions by a new, rapid, relative rate technique
41	Kevin DOUGLAS	Atmospheric oxidation chemistry of meteor ablated phosphorous

42	Atallah EL ZEIN	Temporal variability of polycyclic aromatic hydrocarbons and their oxidative derivatives in Beijing, China: wintertime observations.
43	Layal FAYAD	A New Environmental Simulation Chamber (CHARME) to study the Atmospheric Reactivity and the Metrology of the Environment: Design, Characterization and Preliminary Tests
44	Camille FORTIN	Atmospheric fate of iodomethanol, unimolecular decomposition and its reaction with OH radicals
45	Aline GRATIEN	Analysis of gas-phase and particulate reaction products from high-NO _x photooxidation of n-dodecane: Influence of temperature and relative humidity on secondary organic aerosol formation
46	Fred GRIEMAN	HO ₂ /Acetone Chemistry: Temperature Dependence of Acetylperoxy and Chaperone Mechanism Rate Constants
47	Asma GRIRA	Reactivity of Green Leaf Volatiles (GLVs) in the atmosphere: Kinetics, products and secondary organic aerosol formation
48	Parth GUPTA	Reactivity of a series of alkanes and alkenes with XO radicals (X=Cl, Br and I): A computational study
49	Takashi IMAMURA	OH Radical Formation from the Reactions of Ozone with Dimethyl and Trimethyl Amines
50	Alexander D. JAMES	A novel, low cost material for automotive catalysis
51	Malte JESPERSEN	Theoretical Rate Constants for the 1,4-Cycloaddition of Singlet Oxygen on Conjugated cis-Dienes
52	Revathy KAIPARA	Oxidation of alkyl esters by OH radicals and Cl atoms: An experimental and computational study
53	Carmen KALALIAN	Atmospheric fate of oxygenated biogenic volatile organic compounds
54	Monali KAWADE	A Kinetic Study of Gas Phase OH Radical Reaction with 2-chloroethyl vinyl ether Using Laser Induced Fluorescence Technique in the Atmospheric Temperature Range
55	Alireza Kharazmi	New Observed Triple Fragmentation Photolytic Pathway of Propanal
56	Dorra KHIRI	Ab initio investigation of thermochemical properties of very-short lived brominated substances (VSLS)
57	Florent KRAVTCHENKO	Development and validation of a new experimental set-up to study reactions between peroxy RO ₂ and HO _x radicals
58	Avinash KUMAR	Kinetic investigations for gas phase reactions of monochlorinated propanes with Cl atoms: Experimental and computational studies.
59	Thomas LEWIS	Contrasting pathways to Iodine Oxide Particle formation in the presence and absence of water
60	Ernesto MARTINEZ ATAZ	SO ₂ -Criegee intermediate reaction's role in the formation of secondary organic aerosols
61	Ernesto MARTINEZ ATAZ	Atmospheric Sinks of Styrene: Rate Coefficient and Mechanism of the Cl Atoms Initiated Degradation.

62	Max MCGILLEN	Direct Studies of Criegee Intermediate Reactions Using Cavity Ring-Down Spectroscopy
63	Zara MIR	CH ₂ OO Criegee Intermediate UV Absorption Cross-Sections and Self-Reaction Kinetics
64	Kristian Holten MØLLER	Alkoxy Radical Bond Scissions Explain the Anomalously Low Secondary Organic Aerosol and Organonitrate Yields From α -Pinene + NO ₃
65	Julien MORIN	Experimental Study of Photosensitized reduction of nitrogen dioxide on corn as a source of nitrous acid
66	Julien MORIN	Photocatalytic paints: improving a new binder to reduce VOCs emission
67	Freja F. OESTERSTROEM	Mechanistic Study of the Reaction of CH ₂ F ₂ with Cl Atoms in the Absence and Presence of CH ₄ or C ₂ H ₆ : Decomposition of CHF ₂ OH and Fate of the CHF ₂ O Radical
68	John ORLANDO	Steady State Continuous Flow Chamber for the Study of Atmospheric Hydrocarbon Oxidation Chemistry under Daytime and Nighttime Conditions – Chamber Characterization and First Results
69	Jari PELTOLA	Time-resolved broadband cavity-enhanced absorption spectrometer for reaction kinetic studies of stabilized Criegee intermediates
71	Andrew RICKARD	Mechanisms for Atmospheric chemistry: Generation, Interpretation and Fidelity - MAGNIFY
72	Michael ROLLETTER	Acetylperoxy Radical Revisited - Spectra, Absorption Cross Sections and Kinetics of the Self Reaction
73	Emmanouil ROMANIAS	Development and validation of a THERMAL Regulated Atmospheric Simulation Chamber (THALAMOS)
74	Antoine ROOSE	Uptake of peroxy radicals on organic aerosols : Development of an Aerosol Flow Tube and molecular-level characterization
75	Dharmendra SINGH	Photochemical degradation and production of polycyclic aromatic hydrocarbons and carboxylic acids in Canadian high arctic aerosols (Alert) before and after polar sunrise
76	Vijayakumar SIRIPINA	Hydroxyl radical initiated photo-oxidation of series of butadienes in troposphere: An experimental and computational study
77	Eloise SLATER	Elevated levels of OH observed in haze events during wintertime in Beijing, and the comparison of radical measurements with both steady state calculations and box model simulations.
78	Thomas SPEAK	OH initiated study of the oxidation of N,N'-Dimethylformamide: evidence for QOOH+O ₂ forming OH

80	Daniel STONE	Unimolecular Decomposition Kinetics of the Stabilised Criegee Intermediates CH ₂ OO and CD ₂ OO
81	Sonia TAAMALI	Unravelling the reaction mechanisms of iodous acid with chlorine atom
82	Mariano Teruel	Products and Mechanisms of the Reactions of a Series of Hydrofluoroalkenes initiated by OH Radicals
83	Lauge THORSEN	Epoxide Formation in the Decomposition of MBO232
84	Carmen Maria TOVAR RAMOS	Rate coefficients for the gas phase reactions of chlorine atoms with a series of epoxy compounds
85	Luís Pedro VIEGAS	Reactivity of hydrofluoropolyethers towards OH: a cost-effective implementation of MC-TST
86	Blair WELSH	Vibrationally Excited Products of Roaming Reactions in the Atmosphere as a Novel Source of Hydroxyl Radicals
87	Frank WINIBERG	Study of key OH + NO _x /NO _z reactions under upper troposphere/lower stratosphere conditions
88	Pierre WINTER	Microcanonical Instanton Rate Theory Applied to Molecular Reactions
89	María ANTIÑOLO	Kinetics of the Atmospherically Relevant Gas-phase Reactions of Allyl Cyanide
90	Alex BRENNAN	An inter-comparison of FAGE and CRDS for the detection of HO ₂ and CH ₃ O ₂ radicals in a simulation chamber
91	Rodrigo G. GIBILISCO	Atmospheric degradation of (E)-4-methoxy-3-buten-2-one and 1-(E)-1-methoxy-2-methyl-1-penten-3-one initiated by OH radicals: Kinetics and reaction products.
92	Rodrigo G. GIBILISCO	Gas-Phase Oxidation of Aromatic Hydrocarbons: A Kinetic Study of the OH Reaction with Methoxybenzenes at Atmospheric Conditions
93	Lei HAN	Rate Constants for the Reaction of OH Radicals with Hydrocarbons in a Smog Chamber at Lower Atmospheric Temperatures
94	Claudiu ROMAN	Gas phase kinetic study of the OH radical initiated oxidation of alkylfurans at atmospheric pressure and 298±2 K
95	Claudiu ROMAN	Temperature dependence kinetic studies by using the newly thermostated ESC-Q-UAIC chamber
96	Mariano Teruel	Kinetics and product distribution of the gas phase reactions of β- ocimene and camphene with Cl atoms at room temperature
97	Khatuna KAKHIANI	Morphology and Reactivity: A DFT Study on curved graphene
98	Julian MÜLLER	Structure-reactivity trend for the ozonolysis of fatty acid monolayers – a molecular dynamics perspective
101	Maxi BURGOS PACI	Photochemistry of (FCO) ₂ at 266nm. UV and IR emission
102	Maxi BURGOS PACI	Photolysis of methyl formate at 248nm, a study on the vibrational relaxation of CO.
103	Gus HANCOCK	Self quenching of NO(A ² Σ _{+): evidence for the formation of NO(a⁴Π)}
104	Nozomu KANNO	Theoretical study for the reaction between hydrazine derivatives with OH

105	Artem KOVALENKO	Studying reaction of N^+ ions with HD using rf 22 pole trap down to 15 K.
106	Thanh Lam NGUYEN	Three-Dimensional Master Equation (3DME) Approach
107	Vladimir ORKIN	High Accuracy OH Reaction Rate Constant Measurements: Studies of Pressure Dependencies
108	Thomas PRESTON	Aminosilanes from co-pyrolysis of silane and ammonia
109	Zhen-Yu TIAN	Catalytic oxidation of CO on perfect and defective CuO and Cu_2O surfaces
110	Raimo TIMONEN	Kinetics of the Reactions of Ethyl, n-Propyl, and n-Butyl Radicals with Molecular Oxygen
111	Thuy Dung TRAN	Isotopic effects in the interaction of D_2O^+ with H_2 and D_2 at low temperatures
112	Ondrej VOTAVA	Detailed reinvestigation of water nuclear spin conversion kinetics in supersonic expansion
113	Fayçal ALLOUTI	Oxydation of a potassium iodide surface by gaseous ozone
114	Witkowski BARTŁOMIEJ	Aqueous-phase oxidation of the monoterpene secondary organic aerosols (SOAs)
115	Raluca CIURARU	Volatile Organic Compounds and Secondary Organic Aerosols from Soil Amendments: laboratory and field comparison
116	Joshua BOOTHROYD	Atomic chlorine generation using a radio-frequency atmospheric pressure plasma for use in the comparative reactivity method
117	Joseph BOZZELLI	Towards Direct Molecular Analysis of Atmospheric Oxidized Mercury
118	Marius DUNCIANU	Development of a mobile photochemical reactor to investigate gas-phase chemistry and aerosol formation in the field
119	Daniel STONE	Time-resolved infrared spectroscopy of reactive intermediates in atmospheric chemistry: Method development and characterisation
120	Thomas SPEAK	An instrument for time resolved HO_2 and OH measurement.
121	Harish CHAKRAVARTY	Application of Chemical Organization Theory to Methane Combustion - A Novel Approach to Identify Hierarchical Structures in Dynamical Combustion Networks
122	Rachid HADJADJ	Detailed molecular network of CO_2 hydrogenation
124	Anjitha S. KUMAR GEETHA	Pyrolysis of silanes and silane mixtures - kinetic modelling and experiments using a benchtop reactor.
125	James Thorpe	mHEAT: a Pragmatic approach to sub-chemical accuracy
126	Nicolas VIN	A study of chlorobenzene pyrolysis
127	Fiona WHITING	Hydroxyl Radical Production from Reactions of O_2 with six C_3 – C_5 Acyl Radicals

Oral presentations

Monday, July 23rd, 2018

ASSOCIATIONS REACTIONS: MY ASSOCIATIONS WITH PROF. IAN W.M. SMITH

A. Ravishankara ^{1,*}, M. Pilling ²

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Abstract

Association reactions, where two molecules come together to form a new molecule, play key roles in gas phase reactions taking place in the atmosphere (Earth and elsewhere) and combustion systems. Association reactions are intimately related to the thermal decomposition of molecules since the dissociation reaction is the reverse of the association reactions. Prof. Ian W.M. Smith was a pioneer in understanding association and dissociation reactions through experimental and theoretical work.

In this talk, we will explore the reactions of radicals with molecules where they form adducts of different bond energies- from strong bonds where a brand new molecule is formed to very weak bonds where the course of the reaction is altered. In particular, we will note a very clever idea introduced by Prof. Smith of vibrational relaxation being a measure of the high-pressure limiting rate constant for an association reaction. In addition, the consequences of weak association adducts, ranging from a few kJ/mol to much stronger bonds will be explored. The atmospheric implications of these findings will also be explored.

*In association with Prof. Michael Pilling of University of Leeds.

CRESUSOL, A NEW INSTRUMENT FOR DETERMINING KINETICS AND BRANCHING RATIOS OF ELEMENTARY PROCESSES AT LOW TEMPERATURES

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Abstract

Understanding the mechanism of elementary gas phase reactions leading to the formation of molecules and clusters various conditions, especially at very low temperatures (i.e. low collision energies), is of fundamental interest and yields crucial information for modelling gaseous environments encountered in the fields of atmospheric chemistry (of the Earth and other planets) and astrophysics.

We present a new instrument, CRESUSOL, developed by the Laboratory Astrophysics group at the Institute of Physics of Rennes in collaboration with the DESIRS beamline group at SOLEIL. The main scientific aim of this project is to determine in a systematic manner the product branching ratios of reactions at substantially lower temperatures than has been attempted before (< 100 K). Associated aims include the measurement of rate coefficients for a selection of reactions, including dimerization, down to low temperatures.

To achieve this feat, a CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme or Reaction Kinetics in Uniform Supersonic Flow) reactor is associated with a photoelectron-photoion coincidence (PEPICO) mass spectrometer to probe reactants and products of reaction after threshold photoionisation by the VUV beamline of the SOLEIL synchrotron. The original experimental set up will be presented and preliminary results will be shown for (i) the kinetics of dimerization of formic acid HCOOH observed at 50 and 70 K, (ii) the detection of C₄H₂ resulting from the reaction of C₂H with C₂H₂ at 50 K.

FIELD OBSERVATIONS, LABORATORY MEASUREMENTS AND MODEL SIMULATIONS OF Ni ABLATION AND SUBSEQUENT CHEMICAL REACTIONS IN THE EARTH'S MESOSPHERE.

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Abstract

The ablation of meteoroids in the Earth's upper atmosphere results in layers of metal atoms and ions. Here we investigate the ablation of Ni from meteoroids, the chemical processing it undergoes and the resulting metal layers.

Ni layers have been detected in the Earth's mesosphere. Our recent measurements suggest a typical peak density is around 250 – 400 cm⁻³. The Ni layer is broader than the corresponding Fe layer. These recent measurements were conducted at Kühlungsborn using resonance LIDAR at wavelengths of 337 and 341 nm.

Simultaneously, the kinetics of reactions of neutral Ni and Ni⁺ with atmospheric species have been measured in the laboratory in Pulsed Laser Photolysis (PLP) experiments with LIF detection (neutral Ni) and a Fast Flow Tube with mass spectrometric detection (Ni⁺ ions). Ni⁺ reacts relatively fast to form clusters with O₂ and CO₂, while neutral Ni reacts very fast with O₃ to form NiO, when compared with Fe, the most abundant transition metal found in meteoroids. The reactions of NiO with CO and with O₃ to recycle Ni are also comparatively fast, which may help explain the observed extension of the neutral Ni layer to lower altitudes (around 70 km), about 5 km lower than the Fe layer.

Laboratory measurements have also been conducted on the ablation of Ni from meteoroid analogues. Particles from terrestrial meteorites are flash heated under conditions closely reproducing atmospheric meteoric ablation. Ni is more volatile than the most abundant meteoric metals (Fe, Mg and Si) and ablates at altitudes peaking around 85 – 90 km in the atmosphere. Studies of Ni ablation are useful for modelling the ablation of Fe from meteoroids as Fe in the metallic phase is expected to ablate similarly to Ni. These measurements are used to improve the University of Leeds Chemical Ablation Model (CABMOD). This can then model the meteoric input function, that is, the amount of each element being ablated in the atmospheres as a function of altitude.

The meteoric input function and the rate coefficients will be input into the Whole Atmosphere Community Climate Model (WACCM) to enable comparison with the LIDAR measurements. With this combination of laboratory studies and field measurements we are building a detailed picture of the physical and chemical processes producing Ni layers in the mesosphere.

FORMATION OF ALKYL NITRATES FROM SOME MID-SIZED ALKANES

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Abstract

Organic nitrates are central to the formation of ozone at both local and regional scales. Oxidation of alkanes by OH leads to formation of oxygenated VOCs (OVOCs), and organic nitrates, RONO₂.

With increasing activities involving the extraction of oil and natural gas in the United States, alkane chemistry has taken on a renewed importance. Close to source regions, the formation of nitrates sequesters NO_x, and reduces the extent of ozone production. Depending on the fate of the nitrates, the NO_x can either be released (and be available for ozone production downwind) or can be deposited.

It has been known for many years that the yields of organic nitrates, α , increase (1) with the size of the alkane, (2) with increasing pressure, and (3) with decreasing temperature. Yet, these nitrate formation yields remain uncertain, even from fairly simple alkanes. In general, it is thought that the yields of nitrates from secondary RO₂ are roughly twice those of primary and tertiary alkanes, on the basis of data from Atkinson's group, published in the mid to late 1980s [1,2]. However, Cassanelli et al. have shown that the yields of the nitrates from isopentane are largely independent of the structure of the radical [3].

We are undertaking a systematic study of nitrate yields from mid-size alkanes (4-7 carbon atoms, linear and branched). The experiments are conducted in a 47-L stainless steel reactor with in-situ detection by FTIR, and external sampling by GC-FID. We have measured nitrate yields from a number of linear and branched alkanes at room temperature, using authentic standards to characterize the GC retention times and sensitivity where possible. The yields of tertiary nitrates are consistently greater than the secondary nitrates from the same molecule (corrected for site of attack). Analysis of other products gives further insight into the reactions of the alkoxy radicals produced in the reaction.

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RE-EVALUATION OF THE RATE CONSTANT FOR OH + NO₂ – THE EFFECT OF H₂O ON ONE OF THE MOST IMPORTANT ATMOSPHERIC REACTION

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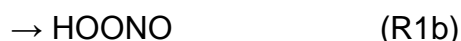
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Abstract

In the atmosphere, the NO_x/NO_y ratio is controlled in part by the radical terminating reaction between the hydroxyl radical (OH) and nitrogen dioxide (NO₂), R1:



In a recent modelling study, Newsome and Evans (Newsome et al., ACP, 17, pp. 14333-14352 (2017)) showed that the uncertainty of 30 % given by evaluation panels (JPL and IUPAC) (Burkholder et al., JPL publications (2015); Atkinson et al., ACP, 4, pp. 1461-1738 (2004)) on the rate constant of this reaction leads to significant uncertainties (10 to 15%) in the prediction of tropospheric OH and O₃ concentrations.

Across relevant atmospheric pressures, the association reaction between OH and NO₂ is in the fall-off regime making prediction to high pressure from low pressure measurements uncertain. Only three previous studies covered the relevant pressure range and bath gas. (Anastasi et al., JCSFT2, 72, pp. 1459-1468 (1976); D'Ottone et al., JPCA, 105, pp.10538-10543 (2001); Mollner et al., Science, 330, pp. 646-649 (2010)).

We measured the rate constant of R1 under pseudo-first order conditions ($[\text{NO}_2] \gg [\text{OH}]_0$) using the pulsed laser photolysis laser induced fluorescence technique. OH was produced from the 248 nm photolysis of suitable precursors (HNO₃ and H₂O₂) while the absolute NO₂ concentration was accurately determined by on-line absorption spectroscopy at several wavelengths.

Using N₂ bath gas we performed measurements in the pressure range 25 to 900 Torr. Our results at $T=295\text{K}$ are consistent with the JPL parameterisation of the rate coefficient (3% higher at 750 Torr) whereas the agreement with IUPAC parameterisation is worse (10% higher).

Most importantly, we find that the rate constant increases significantly in the presence of water vapour with a collision efficiency of H₂O relative to N₂ of 4.5. The implications are that under some atmospheric conditions the rate constant will increase by as much as 30 %. The strong water effect is in accord with the study by Simonaitis and Heicklen (Simonaitis et al., IJCK, IV, pp. 529-540 (1972)) but not with D'Ottone et al. (D'Ottone et al., JPCA, 105, pp.10538-10543 (2001)) who found no water dependence and Sadanaga et al. (Sadanaga et al., CPL, 419, pp. 474-478 (2006)) who found a decrease in k_1 up to 18%.

ROLE OF 2-NITROPHENOL AND METHYL-2-NITROPHENOL PHOTOLYSIS AS MISSING SOURCES OF OH AND HONO IN SOME POLLUTED ENVIRONMENTS: IMPLICATIONS FROM LABORATORY STUDIES

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Abstract

2-Nitrophenol and methyl-substituted 2-nitrophenols are important components of “brown carbon” from biomass burning. Photolysis is their major gas-phase degradation pathway. To determine the extent of light absorptions by 2-nitrophenol (2NP), 4-methyl-2-nitrophenol (4M2NP), and 5-methyl-2-nitrophenol (5M2NP), my group obtained their absorption cross-sections in the 295-400 nm region by using cavity ring-down spectroscopy. We also investigated the HONO, NO₂, and OH formation channels following 308 and 351 nm photolysis of 2NP, 4M2NP, and 5M2NP. Direct NO₂ formation was not observed. The OH quantum yields at 308 and 351 nm were obtained as the ratio of the OH concentration generated in pump/probe laser overlap region to the photon density absorbed by 2-nitrophenol or methyl-2-nitrophenol in the same region; they were 0.69±0.07 and 0.70±0.07 for 2NP, 0.066±0.021 and 0.031±0.017 for 4M2NP, and 0.078±0.038 and 0.042±0.015 for 5M2NP, where uncertainties represent 1σ precision. The average HONO quantum yields at 308 and 351 nm were 0.34±0.09 and 0.39±0.07 for 2NP, 0.26±0.06 and 0.26±0.03 for 4M2NP, and 0.37±0.05 and 0.35±0.06 for 5M2NP. The primary and secondary (i.e., use HONO as secondary OH source) formation rates of OH from photolyzing 10 pptv of 2NP, 4M2NP, and 5M2NP are 3.2×10⁶, 2.3×10⁶, and 3.0×10⁶ molecules•cm⁻³•s⁻¹ (i.e., about 0.47, 0.34, and 0.44 ppbv/hr) at 16.9° zenith angle, while 16.9° zenith angle corresponds to 40°N latitude for July 1 at noontime. In the metropolitan region of Beijing (China), ambient concentrations of methyl-nitrophenols up to 50 pptv have been detected in haze; the measured OH concentrations are significantly higher than predicted values, even after accounting for the contributions of the known OH sources. The larger OH production rate than the OH loss rate and the high aromatic concentrations in the polluted region in China may indeed suggest the existence of unidentified OH sources that can be formed in the atmosphere and photolyzed to generate OH radicals. Results of our study illustrate why gas phase photolysis of 2-nitrophenol and methyl-substituted 2-nitrophenols can drive atmospheric oxidant formation, and why they should be included in models such as Master Chemical Mechanism to close the gap in budgets of OH and HONO for some polluted environments.

INTEGRATED MEASUREMENTS OF ATMOSPHERIC CHEMISTRY: MOVING LABORATORY EXPERIMENTS INTO THE FIELD

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Abstract

Transformations of trace gases in atmospheric models can involve photolytic and both homogeneous and heterogeneous chemical reactions. However, the presence of thousands of atmospheric compounds currently precludes a comprehensive description of their chemistry and challenges the models' capability to predict future changes of atmospheric composition, especially in a context of climate change. Chemical species are often lumped together based on their structure or reactivity and elementary reactions are condensed together to reduce the size of the chemical mechanisms. It is therefore important to test whether these simplified mechanisms can correctly reproduce ambient reactivity.

During the last 15 years, we have witnessed the development of new instruments to probe chemical properties of air masses in the field, including OH, HO₂, O₃, and NO₃ reactivity, O₃ production rates, and potential aerosol mass. Mobile atmospheric chambers are also being developed and deployed in the field to trap and probe the complex oxidation chemistry of ambient air. Comparing field-observations from these new techniques to model-predictions can provide a stringent test of chemical mechanisms implemented in current atmospheric models. In this presentation, the development and deployment of these new tools in the field will be discussed and an emphasis will be put on discussing the potential for improving/validating current atmospheric models.

DEVELOPMENT OF A PHOTO-FRAGMENTATION LASER INDUCED FLUORESCENCE INSTRUMENT FOR THE MEASUREMENT OF NITROUS ACID

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Abstract

The hydroxyl radical (OH) is the primary oxidant in the atmosphere with its concentration determining the lifetime of many species and its reaction with volatile organic compounds (VOCs) leading to the production of secondary organic aerosols and tropospheric ozone. It is important, therefore, that the sources of OH are well understood. Nitrous acid (HONO) has been shown to be a dominant source of OH in urban regions, where daytime concentrations of HONO can reach several hundred pptv. Models, however, currently under-predict HONO concentrations in the day, indicating a missing HONO source

Two possible daytime sources that have been suggested are: Reactive uptake of NO₂ on illuminated surfaces and the photolysis of particulate nitrate.

In order to identify and study these missing sources and determine if they are atmospherically relevant, a photo-fragmentation laser induced fluorescence (PF-LIF) instrument has been built to provide a fast and sensitive measurement of HONO. This instrument is coupled to an aerosol flow tube to measure HONO production from aerosols under illuminated conditions. The PF-LIF instrument measures the OH fragment after the photolysis of HONO.

We will present an overview of the instrument and its development as well as some preliminary results including the production of HONO from illuminated TiO₂ aerosols exposed to NO₂ as well as HONO production from illuminated nitrate aerosols that modelling studies have suggested may explain the levels of HONO observed during the day in the marine boundary layer (Ye et al., Nature, 532, p. 489-491, 2016).

DIRECT DETECTION OF OH RADICALS USING MID-IR 2-f FREQUENCY MODULATION SPECTROSCOPY FOR TEMPERATURE DEPENDENCE STUDIES OF HO₂ + CH₃C(O)O₂

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Abstract

CH₃C(O)O₂ plays an important role in tropospheric chemistry because they are formed from the photooxidation of a large variety of higher carbonyl compounds. In remote regions of the atmosphere where NO_x concentrations are low, the dominant loss pathway for CH₃C(O)O₂ is reaction with HO₂ and other RO₂ radicals.

The title reaction has three possible product channels: HO₂ + CH₃C(O)O₂ → OH + CH₃ + CO₂ + O₂ (R2a), CH₃C(O)OOH + O₂ (R2b), CH₃C(O)OH + O₃ (R2c). The atmospheric impact of the OH channel depends on the overall rate constant and the branching ratios, which together define the formation efficiencies of the organic acid, peracetic acid, and ozone, as well as the re-formation of OH. Large uncertainties in currently reported values of the rate constant and branching ratios warranted further investigation of this reaction.

In this work, we directly detect OH and HO₂ radicals using IR 2-f frequency modulation spectroscopy. Kinetics experiments were conducted in a laser photolysis flow cell using Infrared Kinetic Spectroscopy (IRKS), which combines detection in the IR and UV to monitor multiple species simultaneously in real time. This approach complements prior methods that relied on LIF [1-3] or indirect [4,5] measurements of OH yields. The overall rate constant (k_2) as well the branching ratios of the OH and O₃ product channels (α_{2a} and α_{2c} , respectively) were determined at 100 Torr over a wide range of temperatures (230 - 296 K). This work reports the first temperature dependence measurements of α_{2a} .

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STUDY OF KEY OH + NO_x/NO_z REACTIONS UNDER UPPER TROPOSPHERE / LOWER STRATOSPHERE CONDITIONS

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Abstract

The oxidation of NO_x (NO + NO₂) and NO_z (e.g. HONO₂) species play an important role in the upper troposphere/lower stratosphere (UT/LS). The OH initiated oxidation of NO₂ and HONO₂ play important roles in controlling the O₃ budget, removing HO_x radicals whilst NO_x budgets in the UT/LS. A recent modelling study has highlighted the significance of these reactions in affecting the ozone radiative forcing potential, rating them as the 1st and 9th most important reactions based on the current uncertainty estimation quoted in the JPL Kinetic Data Evaluation. Currently, the recommended uncertainty in $k_{\text{OH}+\text{NO}_2}$ is 30% ($\pm 1\sigma$) and $k_{\text{OH}+\text{HONO}_2}$ is 20% ($\pm 1\sigma$) at STP, but under UT/LS conditions (low T and p), the uncertainty could increase to as much as $\pm 50\%$, which would have a significant impact on atmospheric models. We will present experimental results into the OH + NO₂ and HONO₂ rate coefficient over the matrix of temperature (220 – 300 K) and pressure (25 – 750 Torr) using OH (A ← X) Laser Induced Fluorescence (LIF). Specifically, our results represent the determination of $k_{\text{OH}+\text{HONO}_2}(T,p)$ using two different and complementary in-situ [HONO₂] measurements over an extended pressure range, and the first determination of $k_{\text{OH}+\text{NO}_2}(T,p)$ using in-situ detection of [NO₂]. Experimental results will be discussed along with MESMER calculations and atmospheric impact modelled using the STOCHEM-CRI global model.

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RECENT PROGRESS ON HYDROPEROXIDE CHEMISTRY DURING GAS-PHASE OXIDATION OF FUEL COMPONENTS

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Abstract

Hydroperoxides have a determining role in atmospheric reactions, as well as in liquid and gas-phase oxidation chemistry. This is particularly true concerning the gas-phase chemistry involved in internal combustion engines. Since 2010, using a new type of experimental set-up coupling a jet-stirred reactor to recent techniques of time-of-flight mass spectrometry and infrared cavity ring-down spectroscopy, notable progress has been made in the detection and quantification of hydroperoxides important in combustion environments, such as hydrogen peroxides, alkyl, alkenyl, and keto hydroperoxides. Significant advances in the understanding of the chemistry related to hydroperoxides has also followed the simultaneous detection of carboxylic acids, diones, and hydroperoxides with 4 or 5 oxygen atoms, e.g. the development of models including a third O₂ addition.

USING OH AND HO₂ RADICALS AS MARKERS OF BIOFUEL IGNITION PROPERTIES

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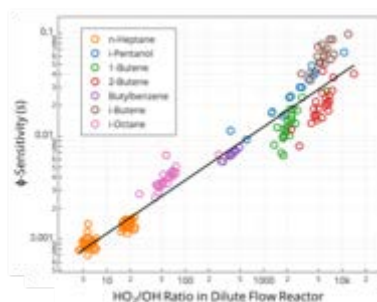
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Abstract

Renewable biofuels and efficient engines are currently being explored in tandem towards the overall goal of a carbon neutral future. However, predictive modeling of the combustion performance of new fuels in advanced engines is still a distant ideal. Historically, ignition delay times (IDT's) measured in a shock tube or rapid compression machine (RCM) have served as the figure-of-merit for fuel performance under set conditions. However, neither shock tubes nor RCM's are well-suited to characterize small quantities of low-volatility biofuels under the low-temperature (T) conditions of interest to advanced compression ignition engines.

We propose a new way to predict the autoignition propensity of fuels based on the assumption that there is a meaningful correlation between fundamental reactivity at low-T (<800 K) and bulk combustion metrics. To test this idea, we have simulated OH and HO₂ profiles in a dilute flow reactor and IDTs in a shock tube, looking for correlations between the two data sets. For example, Figure 1 shows that higher HO₂ to OH ratios measured in the dilute reactor are predicted to correlate with greater sensitivity of IDT to equivalence ratio, under engine conditions (greater -sensitivity). The correlations that were found can be rationalized by simple kinetic models. Encouraged by our simulated results, we are currently building a new experimental tool that is capable of generating such data using flash photolysis coupled with FAGE (fluorescence assay by gas expansion) detection.



ON THE REACTION KINETICS OF DIENES WITH OH RADICALS

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Abstract

In recent years, there has been a lot of interest on engine-fuel design optimization due to increasingly stringent emission regulations. Octane sensitivity of a fuel is an important factor for engine-fuel correlation which measures how a fuel responds to changes in engine conditions. Unlike paraffins, olefins-including dienes (C_nH_{2n-2})-have relatively high octane sensitivity due to the presence of double bond(s). At mild combustion, dienes are likely to undergo addition reactions as opposed to H-abstraction with combustion radicals such as OH, and consequently suppressing the low-temperature combustion pathways.

In this work, we have measured the rate coefficients for the reaction of OH with 1,3-butadienes, cis-1,3-pentadiene and trans-1,3-pentadiene over a wide range of experimental conditions ($T=294-468$ K and $P\sim 0.048$ bar; $T=881-1348$ K and $P\sim 1.5$ bar). We obtained the low-T data in a flow reactor using laser flash photolysis and laser induced fluorescence technique; whereas the high-T data were obtained behind reflected shock waves using UV laser absorption spectroscopy of OH radicals. At low temperatures, we observed differences in the reactivity of cis- and trans-1,3-pentadiene; whereas under shock tube conditions these two isomers exhibited quite similar reactivity indicating fast isomerization before reacting with OH. At low temperature, we found a negative temperature dependence for these dienes + OH reactions revealing that addition channels prevail opposite to high-T where hydrogen abstraction pathways dominate.

Oral presentations

Tuesday, July 24th, 2018

STRUCTURE ACTIVITY RELATIONSHIPS FOR ATMOSPHERIC MODELS: CURRENT STATUS AND FUTURE OUTLOOK

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Abstract

Atmospheric models are important tools to understand the formation and composition of air pollution and to develop policies that reduce the impacts of emissions on air quality and health. Increased computational power, improved computational methods, and progress in understanding of atmospheric chemistry are enabling increasingly sophisticated treatments of chemistry in atmospheric models. Comprehensive mechanisms that incorporate our emerging knowledge of the underlying basic chemistry and give predictions that can be tested by observations are critical in providing confidence in models and pointing to future research needs. It is impractical to conduct laboratory studies of the chemistry of the thousands of multifunctional intermediate oxidation products generated in state-of-the-art gas-phase chemical mechanisms. The chemistry of these species needs to be estimated using structure activity relationships (SARs) which are validated using laboratory measurements for key species. We discuss the status and limitations of SARs, experimental and theoretical data needed to support their development, and future outlook.

FATE OF PEROXY RADICALS IN ATMOSPHERE, COMBUSTION, AND EVERYWHERE IN BETWEEN

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Abstract

Organic peroxy radicals, key intermediates in organic oxidation processes, play central roles in both combustion systems (in which they are responsible for negative temperature coefficients of alkane fuels) as well as the Earth's atmosphere (in which they have a governing influence on HOx cycling, ozone production and aerosol formation). While the chemistry of peroxy radicals in each system is generally understood, the generalized behavior of peroxy radicals across the full range of possible reaction conditions has never to our knowledge been explored. This work uses simulations of pressure-dependent peroxy networks to examine peroxy behavior spanning a wide range of atmospheric and combustion conditions (250-1250 K, 0.01-100 bar, 1 ppt-100 ppm NO), for both unfunctionalized and functionalized peroxy radicals. Results provide insight into major features and impacts of peroxy chemistry in different regimes, including the role of NOx in controlling the negative temperature coefficient regime in combustion and the factors controlling the competition of isomerization with bimolecular channels under atmospheric conditions.

AN ASSESSMENT OF STRUCTURE-ACTIVITY RELATIONSHIP PERFORMANCE IN PREDICTING THE GAS-PHASE RATE COEFFICIENTS OF ORGANIC COMPOUNDS WITH HYDROXYL, OZONE, NITRATE AND CHLORINE

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Abstract

Structure-activity relationships (SARs) are the principle resource for estimating rate coefficients that have not been measured experimentally. With the advent of large, near-explicit oxidation schemes, especially those that are automatically generated,^{1,2} the need for estimation techniques has increased dramatically. Notwithstanding, few studies are available that assess the applicability, accuracy and predictiveness of SAR estimates. In this study, we estimate organic compound oxidation rate coefficients by hydroxyl, ozone, nitrate and chlorine. For this purpose, we have compiled a large database that contains kinetic data for over 1100 compounds. By combining this large sample size together with a diverse range of estimation methods, we present a rigorous test of SAR performance that affords several insights: notably, which functionalities are poorly predicted, which species would benefit most from additional laboratory measurements, and whether an ensemble approach can yield a more robust prediction of chemical reactivity.

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VALIDATION AND EXTENSION OF A STRUCTURE-ACTIVITY RELATIONSHIP FOR REACTIONS OF CRIGEE INTERMEDIATES

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Abstract

Carbonyl oxides (Criegee intermediates, CI) are important intermediates in the ozonolysis of volatile organic compounds (VOCs) in the atmosphere, where part of the CI are formed with thermal energy content. These stabilized CI (SCI) have attracted much attention in recent years, where recent theoretical, experimental and modeling studies find that SCI mostly react unimolecularly or with water vapour (H_2O and $(\text{H}_2\text{O})_2$) in the troposphere, with steady-state SCI concentrations below 10^5 molecule cm^{-3} (Vereecken et al., PCCP, pp. 31599–31612 (2017) ; Novelli et al., ACP, 7807–7826 (2017) ; Khan et al. ESPI, 437–453 (2018)).

A recent study in our research group (Vereecken et al., 2017) presented extensive structure-activity relationships (SARs) for the unimolecular reactions of SCI, and their bimolecular reactions with H_2O and $(\text{H}_2\text{O})_2$, applying these SARs to field data and incorporating them in an atmospheric chemical model. The fate of SCI depends strongly on the substitution patterns, yet several of the substitution patterns encountered in the atmosphere were not included explicitly in the original SAR training set, thus relying on reactivity trend predictions, and on simplifications of the molecular structure. We present a series of new theoretical calculations for additional combinations of substituent types, some covered in the SAR but only by extrapolation of reactivity trends, but also for new substituents such as $-\text{ONO}_2$, $-\text{OOH}$, $-\text{OR}$, and $-\text{OH}$ in various position relative to the carbonyl oxide moiety.

These calculations reliably extend the SAR to a wider range of compounds relevant to the atmosphere. More importantly, though, these additional calculations constitute a validation data set allowing more rigorous error analysis of the earlier SAR, which is rarely available in the literature. Uncertainties are quantified for substitution patterns within the original SAR scope of applicability (i.e. with substituents included explicitly in the SAR) but outside its original training data set. We also examine uncertainties induced by the molecular simplifications that were applied to allow application of the SAR beyond its scope of applicability (i.e. to substituents not included in the training data set).

KINETICS OF CRIEGEE INTERMEDIATES

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Abstract

Reaction of ozone with unsaturated hydrocarbons would produce very reactive Criegee intermediates, which are relevant in atmospheric chemistry, including OH radical formation, oxidation of atmospheric gases like SO₂, NO₂, volatile organic compounds, organic and inorganic acids, and even water. We have investigated the reaction kinetics of various Criegee intermediates (CH₂OO, anti- and syn-CH₃CHOO, (CH₃)₂COO) by using time-resolved UV and IR absorption spectroscopy. We found that there are strong structure dependences of Criegee intermediates in their thermal decomposition and reactions with water vapor (monomer and dimer), alcohol, etc. Our results indicate the following. Syn and dialkyl-substituted Criegee intermediates would thermally decompose to release OH radicals; this reaction involves hydrogen atom transfer and has a large isotope effect. Anti and simplest Criegee intermediates would be consumed by reactions with water vapor in the troposphere.

In addition, the pro and cons of various spectroscopic methods in probing Criegee-intermediate kinetics will be discussed.

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ROOOH: THE MISSING PIECE OF THE PUZZLE FOR OH MEASUREMENTS IN LOW NO ENVIRONMENTS

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Abstract

Field campaigns have been carried out 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 up to a factor of 10 higher than predicted by models and were interpreted as a major lack in our understanding of the chemistry of biogenic hydrocarbons.

In the following years, and until today, many experimental and theoretical studies have been carried out to improve the knowledge of the oxidation mechanism of biogenic VOCs under low NO conditions in order to bring into agreement model and measurement. Some new reaction paths have been found able to recycle OH radicals under low NO, especially for isoprene, but strong disagreement between measurements and models still persists.

Potential interferences in the OH concentration measurements have also been tested using an OH scavenger in FAGE instruments and significant signal have been measured, with the intensity increasing with decreasing NO concentration.

We will present here convincing experimental and modeling evidence that the disagreement between model and measurement is due to interference by the unexpected decomposition of a new class of molecules, ROOOH, during expansion within the FAGE instruments. ROOOH is the product of the reaction between peroxy radicals and OH radicals. Including ROOOH reflects the missing piece of the puzzle in our understanding of OH in the remote atmosphere.

INVESTIGATIONS OF OH RECYCLING IN THE ISOPRENE + OH REACTION IN THE PRESENCE OF OXYGEN: SHEDDING LIGHT ON THE MISSING OH

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Abstract

Isoprene comprises about 40% (~500 Tg C/yr) of global VOC emissions. Because of its high emission rates and rapid reaction with OH radicals ($k \sim 1.01 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K) (R Atkinson, JPCRD, 26, pp. 1329-1499 (1997)), it was expected that isoprene would consume considerable amounts of these radicals. However, a large discrepancy is noticed between the concentrations of hydroxyl radicals estimated by current models and the ones observed in several campaigns performed in known isoprene-abundant areas, such as the Amazon Basin and Borneo ($[\text{OH}]_{\text{measured}}/[\text{OH}]_{\text{model}} \sim 10$) (MM Bela et al. ACP, 15, pp. 757-782 (2015); LK Whalley et al. ACP, 11, pp. 7223-7233 (2011)). These comparisons evidence significant OH radical propagation from the isoprene oxidation. In order to elucidate these radical-recycling processes, Peeters et al. proposed the *Leuven isoprene mechanism* (LIM1), where they present new pathways for regeneration of OH radicals involving peroxy radicals (J Peeters. JPCA, 38, pp. 8625-8643 (2014)).

To clarify the isoprene oxidation process, laser flash photolysis experiments with detection by laser induced fluorescence (LFP-LIF) were performed as a function of temperature (298 – 730 K), in the presence and absence of oxygen, using both a conventional LFP-LIF instrument and a recently-developed instrument capable of measuring the fast kinetics of radicals at high pressures (~2 atm) and temperatures (~750 K).

No major differences were observed in the OH decay traces below 400 K and high concentrations of oxygen ($[\text{O}_2] \leq 1 \times 10^{19} \text{ cm}^{-3}$). However, interesting non-exponential OH traces were observed at temperatures above 400 K; detailed analysis reinforces an excellent agreement between our experimental observations and the LIM1 mechanism. Minor changes in the OH-regenerating energy barriers are made (~1.9 kJ mol⁻¹) and a global multi-temperature raw-trace fitting procedure guarantees the agreement with previous chamber measurements of HPALDs. The impact of these findings on atmospheric modelling was evaluated via the Master Chemical Mechanism, being 40 % of the missing OH in the OP3 campaign elucidated (LK Whalley et al. ACP, 11, pp. 7223-7233 (2011)). Finally, the analysis reveals the existence of an OH recycling route in a long timescale ($t > 1 \text{ ms}$), consistent with the decomposition of DIHPCARP species.

SPECIATED MONITORING OF ORGANIC PEROXY RADICALS: FIRST LABORATORY APPLICATIONS

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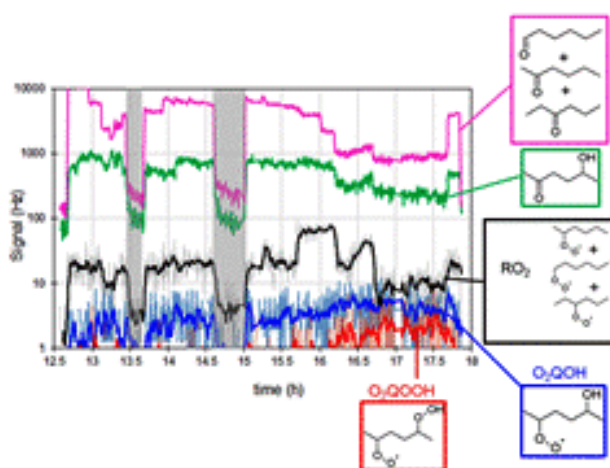
Abstract

Organic peroxy radicals ("RO₂", with R organic) are key intermediates in the oxidation of organic compounds in many chemical systems, such as the Earth atmosphere and combustion engines. For decades, the lack of detection technique distinguishing different RO₂ ("speciated" detection) has been a major limit to the understanding of their reaction mechanisms, as many different RO₂ with different reactivity are often present simultaneously in these systems. A mass spectrometric technique based on proton transfer ionization has thus been developed for the speciated detection of oxygenated organic radicals. Its first applications to the investigation of atmospherically-relevant RO₂ reactions in laboratory will be presented, such as:

- an investigation of the cross-reactions between different radicals (CH₃O₂, CH₃C(O)O₂, c-C₆H₁₁O₂, and (CH₃)₃CO₂) where, for the first time, each radical was monitored individually and in real-time, and their consumption by the cross-reaction was observed directly (Nozière and Hanson, *J. Phys. Chem. A*, 212, 8453-8464, 2017),

- an investigation of the autoxidation of n-hexylO₂ in the oxidation of n-hexane at room temperature, where the initial radicals and those produced by autoxidation (O₂QOOH and O₂QOH) were observed directly (Fig. 1) and allowed to determine the autoxidation rates.

These examples will show how this new technique can improve the understanding of RO₂ reactions.



ASTROCHEMISTRY: MOLECULE FORMATION AT THE FRONTIER OF PHYSICS

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Abstract

The interstellar medium (the space between the stars) is not only cold ($\sim 10 - 100$ K) and tenuous ($\sim 10^2 - 10^8$ particles cm^{-3}), it is also permeated by far-ultra-violet photons (\sim eV) from hot stars and energetic cosmic rays (\sim GeV) accelerated by dying stars. As such, it might be expected that this is a particularly harsh environment for molecule formation and survival because, in the words of Sir Arthur Eddington in 1926, "... when once a molecule becomes dissociated there seems no chance for the atoms to join up again". We now know that the opposite is true: molecules are found everywhere in space, and the interstellar medium exhibits a rich and exotic chemistry that is quite unlike anything that exists naturally here on Earth. The discipline of "Astrochemistry" brings together theorists, experimentalists, and observers to study and better understand the mechanisms that control the molecules found in space, and to determine how observations of molecular emission can be used to constrain the physics of the host environment. Because of the cold and tenuous nature of most astrophysical environments, the chemistry is inherently out of equilibrium, and time-dependent (kinetic) chemistry sets the abundances and distribution of molecules. In this talk I will review what is known about gas-phase chemistry in space from the past ~ 70 years of study, from the perspective of an astrochemical modeller.

ULTRA-LOW TEMPERATURE KINETICS OF THE OH-REACTION WITH OXYGENATES IN THE INTERSTELLAR MEDIUM

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Abstract

Dense molecular clouds of the interstellar medium (ISM) are chemically rich regions of space where stars are formed. In the late 1960s and early 1970s, small oxygenated species, such formaldehyde (H₂CO, Snyder et al., Phys. Rev. Lett. 22, pp. 679–681 (1969)), methanol (CH₃OH, Ball et al., ApJ, 162, pp. L203-L210 (1970)) and ethanol (CH₃CH₂OH, Zuckerman et al., ApJ, 196, pp. L99–L102 (1975)) have been detected in diverse astrophysical environments. The hydroxyl (OH) radical is ubiquitous in the ISM and it was first detected in 1963 (Weinreb et al., Nature, 200, pp. 829-831 (1963)). In order to interpret the abundances of these oxygenates observed by radioastronomy, astrochemical models need the rate coefficients, $k(T)$, of the processes in which they are involved at the temperatures of the ISM (~10-100 K). Recent experiments performed in our laboratory showed a significant increase of $k(T)$ at ISM temperatures for the OH-reactions with H₂CO (Ocaña et al. ApJ. 850, pp. 2017), CH₃OH (Antiñolo et al., ApJ. 823:25, pp. 1-8, 2016), and CH₃CH₂OH (Ocaña et al., PCCP, 20, pp. 5865-5873, 2018). Ultra-low temperatures are achieved in the laboratory using the pulsed and continuous CRESU (French acronym for reaction kinetics in a uniform supersonic flow) technique (Jiménez et al., Rev. Sci. Instrum. 86:045108, pp. 1-17, 2015). The pulsed laser photolysis of H₂O₂ was used as a source of OH radicals in the jet and the laser induced fluorescence technique was used to monitor their temporal evolution. The kinetic data of the OH-reactions with H₂CO, CH₃OH and CH₃CH₂OH were obtained between 11.7 K and 150 K. The impact of the high OH-reactivity of H₂CO and CH₃OH will be discussed in terms of its role on the gas-phase formation of HCO and CH₃O radicals in dense molecular clouds. In addition, the effect of the gas density on $k(T)$ was explored for several temperatures, particularly for CH₃CH₂OH. For the OH+CH₃CH₂OH reaction, Caravan et al. (JPCA, 119, pp. 7130-7137, 2015) observed a significant pressure dependence of $k(T)$ around 85 K and 140 K. In this work, we elucidate this potential dependence of $k(T)$ with total pressure.

LOW TEMPERATURE GAS PHASE REACTION RATE COEFFICIENT MEASUREMENTS: TOWARD MODELING OF STELLAR WINDS

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Abstract

Stellar winds of Asymptotic Giant Branch (AGB) stars are responsible for the production of ~85% of gas molecules in the interstellar medium, and yet very few of the 10 – 300 K reaction rate coefficients needed to model the production and loss of these molecules have been experimentally measured. Furthermore, the few measured rate coefficients often vary from predicted values by orders of magnitude due to an inverse temperature dependence of reaction rate coefficients observed below ~300 K. This non-Arrhenius behavior of reaction rate coefficients at low temperatures can be caused by the formation of long lived pre-reaction complexes and quantum mechanical tunneling through the barrier to reaction.¹

Reaction rate coefficients that were predicted to produce the largest change in the production/loss of Complex Organic Molecules (COMs) in stellar winds at low temperatures were selected from sensitivity analysis. Here we present measurements of rate coefficients using a pulsed de Laval nozzle apparatus with the Pump Laser Photolysis - Laser Induced Fluorescence (PLP-LIF) technique. Gas flow temperatures between 43 – 134 K have been produced by the University of Leeds apparatus through the controlled expansion of N₂, Ar, or He gas through de Laval nozzles of a range of Mach numbers between 2.49 and 4.25.^{2,3}

Reactions of interest include those of ¹CH₂ and OH with volatile organic species, in particular formaldehyde. Kinetics measurements of these reactions at low temperatures will be presented using the decay of the reagent. Products have been observed in some cases (e.g. H atoms from CH₂ reactions) and work is in progress to observe others. The ability to monitor both reactants and products is desirable in cases where it is necessary to determine the branching ratio between quenching and reaction of electronically excited reactants (e.g. ¹CH₂) or to measure branching ratios of multiple product pathways. Since formaldehyde and the formal radical (HCO) are potential building blocks of COMs in the interstellar medium, low temperature reaction rate coefficients for their production and loss can help to predict the formation pathways of COMs observed in the interstellar medium.

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MULTIPLEX SYNCHROTRON VUV PHOTOIONIZATION METHODS FOR RADICAL REACTIONS IN ATMOSPHERIC CHEMISTRY: CH₃ + O₂

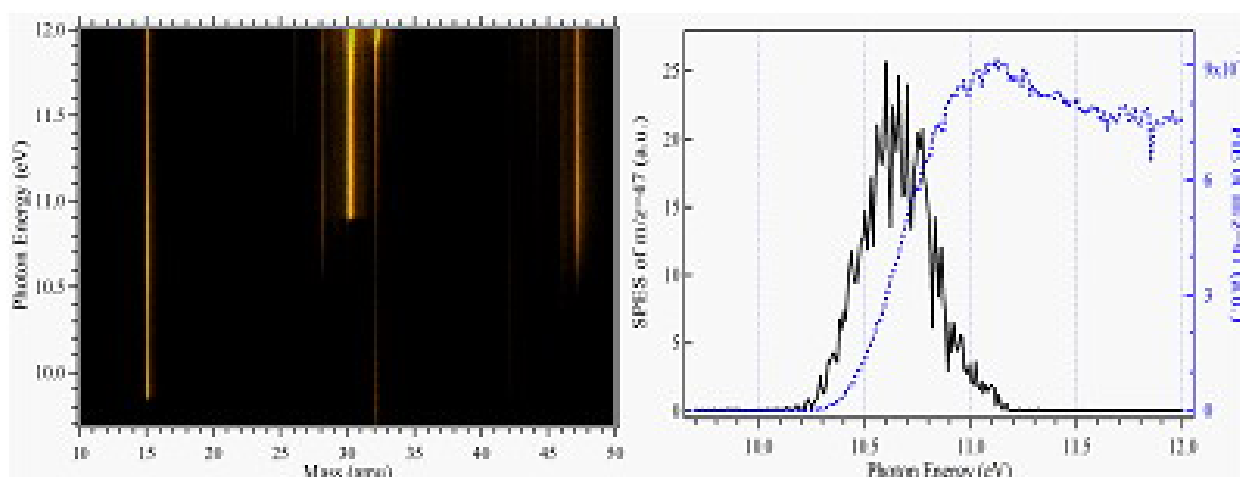
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Abstract

We will present multiplex synchrotron photoionization approaches, double imaging photoelectron photoion coincidence spectroscopy (i²PEPICO) and photoionization mass spectrometry (PIMS), coupled with a microwave discharge flow tube and tunable vacuum ultraviolet (VUV) synchrotron radiation at SOLEIL, France and NSRL, China to investigate free radical reactions in atmospheric chemistry. In particular the i²PEPICO scheme provides a novel strategy to obtain pure photoelectron spectra of products without contamination from other byproducts and a multiplex and universal detection where high sensitivity and selectivity is achieved. As a representative example, the CH₃ and O₂ reaction has been selected and investigated in detail in experiments. The products towards different reaction pathways, together with some minor products from secondary reactions in the flow tube, have been simultaneously determined from the mass-selected threshold photoelectron spectra (TPES) and photoionization efficiency spectra (PIES), including identification of isomeric or isobaric products.



PHENYL RADICAL ADDITION TO UNSATURATED HYDROCARBONS: PRODUCT DISTRIBUTIONS & RATES

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Abstract

Using a unique flash photolysis apparatus combining photoionization laser absorption spectrometry (LAS) and time-of-flight mass spectrometry (TOF-MS), accurate kinetics of phenyl radical reactions with ethylene, propylene, and acetylene were measured by LAS, and product branching within the corresponding reaction networks were quantified by TOF-MS.

The reaction kinetics of phenyl radical with ethylene has been previously investigated (297-523 K) with cavity ring-down spectroscopy, and the product branching has been predicted by quantum chemical calculations without experimental measurement. In the present work, the reaction kinetics and the branching ratios for primary chemistry products were measured up to 800 K. As temperature increases, the appearance in the TOF-MS of the H-loss product and the H-abstraction product changes the product distribution, which is dominated by radical adducts at low temperature.

In the phenyl radical + propylene reaction network, four products which were expected from previous calculations of the potential energy surface (PES) were all quantified with our apparatus. Unexpectedly, a fifth product, benzyl radical, was observed and accounted for ~10% of the branching at 700 K. To rationalize the presence of benzyl radical, a new reaction pathway involving an aromatic-catalyzed 1,2-H migration was discovered using theoretical calculations, and the revised PES agrees well with the TOF-MS measurements.

The phenyl + acetylene reaction demonstrates hydrogen abstraction-acetylene addition (HACA) in the simplest manner by forming naphthalene; however, no experimental studies have reported the time dependence of products. The temporal profiles measured by TOF-MS distinguish the formation of products from the first and the second acetylene addition. With the help of Reaction Mechanism Generator, a reaction mechanism was developed and compared with the experimental results.

References:

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INVESTIGATIONS INTO THE REACTION OF CYCLOPENTADIENE WITH CH RADICALS: A NOVEL ROUTE TO BENZENE FORMATION

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Abstract

Cyclopentadiene has been detected in many high temperature reactions and has recently been identified as a major product during the pyrolysis of jet fuel JP-10. (Long Zhao, T.Y., Kaiser, R.I., et. al. Phys. Chem. Chem. Phys., 19, 15780 (2017)) Experimental and theoretical investigations into its reaction with abundant CH radicals is necessary to understanding the initial step of aromatic ring formation of polycyclic aromatic hydrocarbons (PAHs) in combustion environments. In this study, experimental kinetic rate constants are obtained using a pseudo-1st order approximation over the 298-450K temperature range and at a pressure of 5 Torr in a quasi-static reaction cell using pump-probe laser spectroscopy. Isomer-resolved product detection and branching ratios are measured at room temperature for the reaction using multiplexed photoionization time-of-flight mass spectrometry coupled to synchrotron radiation at the Advanced Light Source in Berkeley, California. DFT methods and CBS-QB3 level of theory are used to calculate the potential energy surface (PES) for the reaction. It is found that the CH radical can undergo barrierless cycloaddition along the C=C bonds or insertion into a C-H bond to form C₆H₆ isomer products and a H atom. Master-Equation calculations using the MESMER program are performed to infer product branching ratios about the products. (Glowacki, D.R., et. al. J. Phys. Chem. A., 116, 9545-9560 (2012)) At room temperature and 5 Torr conditions, the calculations suggest benzene is the main reaction product (>95%). Extrapolation of the kinetic information using these methods to higher, combustion relevant conditions (T > 1500K, P > 760Torr) is also discussed. These investigations support the experimentally fast reaction rate through the main entrance channel of barrierless CH radical cycloaddition to produce benzene. In order to provide a detailed and precise analysis of the reaction mechanism, Bonding Evolution Theory (BET) is applied to the calculated PES. BET uses topology to analyze the electron localization function and Thom's catastrophe theory and allows for monitoring of the flow of electron density during chemical rearrangement. (Andrés, J., et. al. Phys. Chem. Chem. Phys., 19, 29031(2017)) The collaboration of these techniques employed confirms the role of cyclopentadiene in first aromatic ring formation in combustion environments.

THERMAL DECOMPOSITION OF SULFUR COMPOUNDS: KINETIC MODELING AND EXPERIMENTAL VALIDATION

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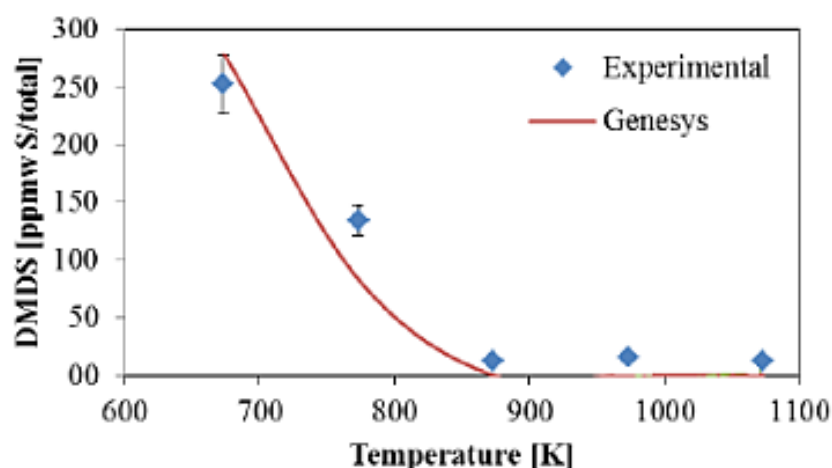
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Abstract

Sulfur-containing compounds play a key role in many industrial processes. In this work, the decomposition of the sulfur-containing steam cracking additive dimethyl disulfide (DMDS) is studied in two-fold. First, experiments are conducted in a quartz flow reactor and both the pure pyrolysis in nitrogen as well as in the presence of hydrocarbons is studied. Second, a kinetic model is constructed using the automatic kinetic model generation tool Genesys (N.M. Vandewiele et al., Chem. Eng. J., 207, pp. 526-538 (2012)). Genesys makes use of user-defined databases containing thermodynamic and kinetic parameters for hydrocarbon and organosulfur compounds calculated with the CBS-QB3 composite method. If data is not available for certain species or reactions, the group additivity method based on these high-level ab initio calculations is applied. The simulated DMDS conversion and major product yields agree well with the experimental data acquired at the bench-scale setup over the studied temperature range. Rate-of-production analysis allows to identify the dominant reaction pathways and intermediates under both pyrolysis and steam cracking conditions. The decomposition of DMDS is mainly initiated by homolytic C-S and S-S bond scission reactions. Once radicals are created, hydrogen abstraction, isomerization and β -scission reactions lead to the formation of the major products methane thiol, carbon disulfide and hydrogen disulfide.



MODELING THE THERMAL DECOMPOSITION OF METHYL ACETATE: A STUDY IN COMBUSTION

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Abstract

In this work, we have modeled the pyrolysis of methyl acetate, CH₃C(O)OCH₃, as a prototype for fatty-acid combustion. We previously studied this molecule in the context of the experimental work of Porterfield et al. [1], and now focus on a high-level kinetics analysis of the chemically significant pathways discussed in that paper.

The potential energy surface of this decomposition features tight/loose transition states, products with complicated electronic structures, and competing pathways. To meet these challenges we employed the mHEAT thermochemical method, which yields total atomization energies to within +/- 0.5 kcal/mol and has successfully described gas phase reactions before [2]. Harmonic vibrational analysis was performed with the CCSD(T)/ANO1 model chemistry, and anharmonic coupling constants were calculated using CCSD(T)/ANO0, both in the frozen-core approximation. These results were used to determine the sum and density of states relevant to kinetics simulation, including anharmonicity, quantum tunneling, and vibrational coupling between the reaction coordinates and the other modes.

We then used a two-dimensional master equation program, which incorporates angular momentum via the "fixed-J" treatment [3], to explore the product branching ratios and rate coefficients of this system at temperatures of 1000-2000 K and pressures of 0.1-100 atm. The Barts-Widom technique was used to obtain phenomenological rate constants.

Our predicted primary products are CH₃OH and CH₂CO formed via two competing pathways, with 2CH₃ and CO₂ as significant, but temperature dependent, secondary products resulting from the decomposition of CH₃ and CH₃CO₂/CH₃OCO. Additionally, we find negligibly small quantities of CH₂O and CH₃CHO. Our analysis is consistent with the experimental results [1]. Interestingly, the formation of methanol and ketene defies chemical intuition and proceeds via a less energetically favorable route due to sum of states (entropic) differences between the competing transition states, validating the use of high-level analysis.

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Oral presentations

Wednesday, July 25rd, 2018

POLLUTANTS EMISSION FROM MODERN CARS AND THEIR CONTRIBUTION TO SOA FORMATION

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Abstract

The demand for urban mobility is steadily increasing and the growing number of vehicles in cities has major environmental consequences. Most of the urban areas in France and around the World suffer from poor air quality which results in increased morbidity and mortality rates among the urban population. Legislative authorities have tried to counteract this problem by imposing stringent emission limits on selected air pollutants, nitrogen oxides (NO_x) and particulate matter (PM), which have been associated with adverse effects on human health. Car manufacturers have responded to these emission regulations by introducing a series of in-engine modifications and exhaust after treatment technologies, e.g. the Diesel Particulate Filter (DPF) or Selective Catalytic Reduction (SCR) of NO_x. We have recently conducted emission measurements on Euro 5 and Euro 6 passenger cars and have observed that, while primary emissions of pollutants subjected to regulations are indeed reduced, other non-regulated pollutants (e.g. organic nitrogen compounds and selected hydrocarbon classes of low volatility) are emitted in substantial quantities. Many of the observed compounds are highly reactive in nature and will be rapidly transformed in the atmosphere potentially contributing to the formation of secondary organic aerosols (SOA).

Car exhaust has been measured at the tailpipe and after processing in dynamic simulation reactors. Primary emissions and oxidation products, both in the gas and the particulate phase, have been analyzed using some of the most advanced on-line mass spectrometry techniques as the newly developed CHARON ("Chemical Analysis of Aerosol Online") particle inlet and a proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS). Complementary studies on selected chemicals found in the exhaust (toluene, octane and cyclohexane) were also carried out for elucidating degradation mechanisms and reaction products under variable experimental conditions (temperature, humidity, seeds surface). First, second and third generation products were observed in the gas phase and a tentative mechanism for their degeneration was established. Particle phase composition and yields were investigated with CHARON.

EFFECT OF DIMERIZATION ON THE OH-INITIATED HETEROGENEOUS OXIDATION OF SACCHARIDE NANOPARTICLES

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Abstract

Sugars (primary saccharides, saccharide polyols and anhydro-saccharides) are water-soluble organic carbon molecules which are a main constituent of atmospheric organic aerosols. Modeling the chemical transformation of such organic aerosols under atmospheric conditions requires a better understanding of the physical and chemical processes governing the multiphase kinetics. In the present study we investigate the OH-initiated heterogeneous oxidation of mixed monosaccharide–disaccharide nano-particles with variable particle viscosities. The decay rates of the saccharides is determined by gas chromatography coupled to mass spectrometry as a function of the OH exposure. The initial particle composition is varied by changing the molar ratio of the monosaccharide and disaccharide. In liquid nano-droplet the monosaccharide is found to decay relatively fast while the disaccharide displays an arrested kinetic behavior. For such well mixed particles, this behavior is likely to be due to the partitioning of the sugars between the interface and the particle bulk (M. L. Pegram *J. Phys. Chem. C.* 113, pp. 2171-2174 (2009)). In semisolid particles, the presence of the disaccharide increases the particle viscosity and slows down the decay rates of both reactants. A reaction-diffusion model is developed in order to evaluate the effect of the composition dependent diffusion on the arrested decay behaviors.

PROBING THE ELECTRONIC STRUCTURES, INTERFACIAL SOLVATION PROPERTIES AND SURFACE PH OF ORGANIC-CONTAINING AQUEOUS NANOAEROSOLS

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Abstract

An in-depth understanding of the fundamental energetic and structural properties at or near the interface of nanoscaled aqueous aerosols is of fundamental and crucial importance in understanding the impacts of organic species, either of biogenic or anthropogenic origins in intervening the cloud formation microphysics and the intrinsic nature of clouds. To address these issues, we applied aerosol VUV photoelectron spectroscopy to investigate the valence electronic structures and interfacial characteristics of pure and several organic-containing aqueous nanoaerosols that are of atmospheric significance. To assess the intrinsic structural and energetic properties of pure water droplets in the nanoscaled size regime and how they may be modified due to the presence of solutes, we studied the VUV photoelectron spectrum of pure H₂O and D₂O nanoaerosols. Both the fully vibrationally-resolved fine structures of gaseous water features and the partially vibrationally-resolved condensed water features were obtained. The partially vibrational resolved photoelectron spectral features of water nanodroplets imply that the condensed water in the form of nanoscaled water droplets may not be entirely disordered. The possible origins for the observed isotopic effect, as well as the micro-hydration structure and nature of water nanodroplets will be discussed. Considering that many organic species emitted from anthropogenic activities may encounter fine water nanodroplets and form aqueous aerosols in the atmosphere, we studied the valence photoelectron spectroscopy of phenol and three dihydroxybenzene isomers including catechol, resorcinol, and hydroquinone aqueous nanoaerosols at varying pH conditions. It reveals that the hydration extents, pH values, deprotonation status, and numbers/relative arrangements of -OH groups are crucial factors affecting the ionization energies of phenolic aqueous nanoaerosols and thus their redox-based activities. The multi-faceted implications of the present study in the aerosol science, atmospheric/marine chemistry, and biological science will be addressed.

COMBINING QUANTUM CHEMISTRY WITH CLASSICAL MOLECULAR DYNAMICS FOR THE THEORETICAL STUDY OF RADICAL REACTIVITY AT THE SURFACE OF ORGANIC AEROSOLS

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Abstract

Models of atmospheric chemistry are widely used to perform projections of future changes in the chemical composition of the global troposphere, including changes in climate related greenhouse gases and aerosol particles. However, large uncertainties are still associated with the chemistry implemented in these models, which in turn can lead to inaccurate long-term predictions.

Complementary to laboratory experiments, computational modelling at the molecular level provides valuable insights on the elementary chemical and physical mechanisms. Although classical molecular dynamics (MD) can provide valuable information on growth, structure or mass accommodation of large systems, it is not possible to describe properly bond breakings involved in reactive processes. On the other hand, a full quantum mechanical treatment is not possible for systems comprising thousands of atoms.

We shall present some results on the study of the reactivity of radicals such as Cl on the surface of organic aerosols composed of long carboxylic acids, using a hybrid Quantum Mechanics/Molecular Mechanics (QM/MM) scheme. The aerosol geometry is obtained from MD simulations using the Gromacs package [1]. The QM part will be treated at the DFT level for the localization of the reactants, products, Van der Waals and transition states, followed by single point CBS/CCSD(T) energies [2]. By sampling the surface of the aerosol, it is possible to obtain an averaged value for the rate constant, leading to an estimation of the reactive uptake coefficient.

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HIGHLY OXIDIZED PRODUCTS FROM RAPID ALKANE AUTOXIDATION PART 1 – IMPLICATIONS FOR ATMOSPHERIC SECONDARY ORGANIC AEROSOL FORMATION

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Abstract

Highly oxidized multifunctional compounds (HOM) from gas-phase autoxidation of volatile organic compounds (VOC) have been implied as a highly efficient direct pathway to ambient secondary organic aerosol (SOA)¹⁻⁴. As opposed to major VOC oxidation pathways leading to sequential fragmentation of the carbon skeleton, autoxidation is a rapid way for molecular growth and subsequent prompt reduction in vapor pressure - a prerequisite for aerosol formation. The reaction chain is mediated by peroxy (RO₂) radical intermediates, and leads to oxidized products with an oxygen-to-carbon ratio as low as 1.5, and practically non-volatile nature²⁻⁴. In endocyclic alkene ozonolysis, HOM formation has been found particularly efficient²⁻⁴, and even aromatic compounds have been recently shown to autoxidize under favourable reaction conditions⁵. Despite these recent findings, almost nothing is currently known about the potential for atmospheric alkane autoxidation, which is an important group of compounds in both atmospheric and combustion systems⁶. In order to resolve if alkanes are able to autoxidize under ambient conditions, we set out to investigate if alkane OH initiated oxidation produces measurable quantities of HOM products.

In the current work, we performed a suite of VOC oxidation experiments of carefully selected precursor compounds under ambient atmospheric conditions. The investigations were performed in quartz flow tube reactors initiating the oxidation sequence with an OH+VOC reaction. OH radicals were produced either by photolysis of H₂O vapor within the flow reactor, or by tetramethylethylene ozonolysis reaction. The highly oxidized products were detected utilizing nitrate (NO₃⁻) chemical ionization mass spectrometry (CIMS). We found out that surprisingly efficient autoxidation takes place in certain alkane oxidation systems, which then allowed us to resolve the important structural aspects of the precursor compounds that aid this process forward.

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HIGHLY OXIDIZED PRODUCTS FROM RAPID ALKANE AUTOXIDATION PART 2 – IMPLICATIONS FOR IGNITION IN COMBUSTION SCIENCE

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Abstract

The advanced combustion engine has the potential to enhance the fuel efficiency and reduce the soot and NO_x emission simultaneously [1, 2]. The core for the combustion process is the auto-oxidation chemistry of fuels, which are driven by the reactions of the peroxy radicals with the successive intramolecular H-atom isomerization and O₂ addition to the radical sites [3, 4]. The literature studies have revealed that at least three stage sequential O₂ addition leads to peroxides that trigger the ignition process by releasing the OH radicals [5].

In the current work, we performed a suite of hydrocarbon oxidation experiments of carefully selected precursor compounds under combustion conditions. The investigations were performed in a jet-stirred reactor at atmospheric pressure. The temperature of the reactor was monitored by an oven from 500-600 K. The products after the reaction were sampled by a quartz probe and detected by utilizing nitrate (NO₃⁻) chemical ionization mass spectrometry (CIMS), the cornerstone of gas-phase highly oxidized products detection during recent years. The highly oxidized products were observed, not only confirming the observation of literature study [5] but also revealing new insights into the auto-oxidation mechanism of hydrocarbons. The structural features of the hydrocarbons on the production of the highly oxidized products were discussed.

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DECOMPOSITION KINETICS FOR HONO AND HNO₂

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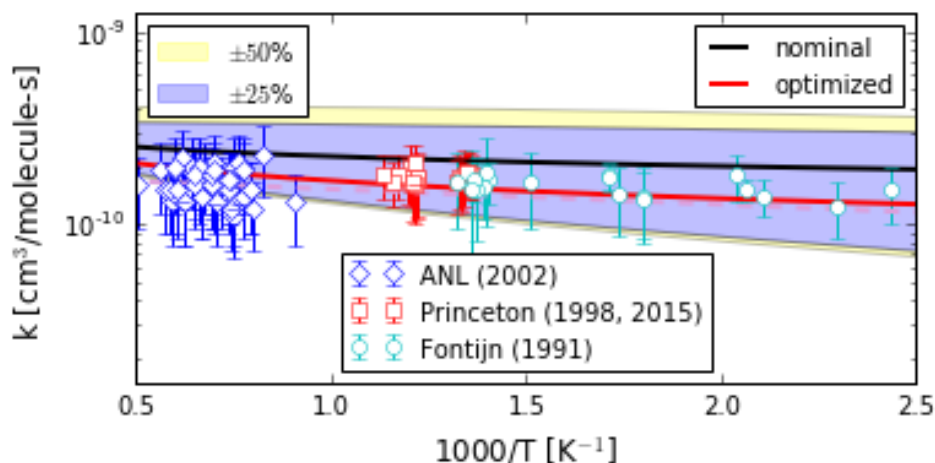
Abstract

Nitrous acid (HONO) and its isomer nitryl hydride (HNO₂) are key intermediates in many gas-phase systems, from atmospheric chemistry to combustion to energetic materials. HONO/HNO₂ chemistry is increasingly relevant in many advanced engine designs that rely on low-temperature combustion. The key contribution of these species is their role in the chain branching sequence:



Thus, quantitative predictions for the rates of formation and decomposition of HONO and HNO₂ are key to predictive models for these engines.

In this talk, we will summarize recent theoretical and computational work to develop an optimized, self-consistent system of temperature and pressure-dependent rate coefficients for the HNO₂ system. The work combines high-accuracy electronic structure theory, variable reaction coordinate transition state theory (VRC-TST), and RRKM/Master Equation methods. A novel component of this work is the inclusion of the barrierless reactions $\text{H} + \text{NO}_2$ and $\text{OH} + \text{NO}$ within a multi-scale informatics (MSI) framework, which allows us to optimize the interaction potential within the estimated uncertainty limits of the multi-reference methods against experimental data. The resulting system of optimized rate coefficients are in excellent agreement with all available experimental data for $\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$ and $\text{OH} + \text{NO} \rightarrow \text{HONO}$. The new rate constants are compared to prior literature values. For the case of HNO₂ kinetics, all prior mechanisms fail to include the most important kinetic pathway.



KINBOT: AUTOMATED STATIONARY POINT LOCALIZATION ON POTENTIAL ENERGY SURFACES

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Abstract

The exploration of a potential energy surface for the identification of all kinetically significant stationary points, especially saddle points (SPs), to enumerate all reaction possibilities of a molecule in a chemical process remains a challenge. Many manual steps are still required to go from a chemical reaction to its rate coefficient including the construction of species geometries or good initial guesses for transition state, the verification of results by visualizing normal modes, etc. To automate this process, a new version of our software tool called KinBot is being developed. KinBot starts from a simple line notation of a molecule, i.e. a SMILES, and searches for all reaction pathways of that molecule. First, the line notation is converted to 3D coordinates of the atoms in the molecule. To search for reaction possibilities, KinBot recognizes molecular functionalities and iteratively changes the reactant geometry towards an initial guess of the transition state based on known SP geometries, and is subsequently used in a SP optimization by a third-party quantum chemistry code. Additionally, KinBot searches for the lowest energy conformers, performs hindered rotor scans, and spawns high-level single point electronic energy calculations. The output of KinBot is written in an input file for the MESS master equation calculation code (Y. Georgievskii et al., *J. Phys. Chem. A*, 117 pp. 12146-12154 (2013)) to obtain pressure- and temperature-dependent rate coefficients.

KinBot has been used to identify all the reactions on the OH+C₃H₆ potential energy surface, because this surface has been extensively studied in the past (J. Zádor et al., *PCCP*, 11, pp. 11040 – 11053 (2009)). KinBot automatically located all of the previously found transition states, except for the two entrance channels. Additionally, KinBot found high-energy water elimination and cyclization reactions as well as one low-energy isomerization not previously reported.

To also show the capabilities of KinBot for closed-shell systems, the potential energy surfaces of gamma-valerolactone (GVL) and 4-pentenoic acid have been reproduced and compared to the literature (R. De Bruycker et al., *Proc. Combust. Inst.*, 35, pp. 515 – 523 (2015)). These molecules show interesting molecular pathways which KinBot found, especially the ring opening from GVL to 4-pentenoic acid, i.e. the main decomposition route of GVL below 1000K.

HIGH-LEVEL MULTI-REFERENCE WAVE FUNCTION AND DENSITY FUNCTIONAL THEORY TREATMENT OF THE N₂H₃ + NO₂ REACTION

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Abstract

The N₂H₃ + NO₂ reaction plays an important role during the early stages of hypergolic ignition between N₂H₄ and N₂O₄. Here for the first time, the reaction kinetics of N₂H₃ in excess NO₂ was studied in 2.0 Torr of N₂ and in the temperature range 298-348 K in a pulsed photolysis flow-tube reactor coupled to a mass spectrometer. The temporal profile of the product, HONO, was determined by direct detection of the m/z +47 ion signal. For each chosen [NO₂], the observed [HONO] trace was fitted to a bi-exponential kinetics expression, which yielded a value for the pseudo-first-order rate coefficient, k', for the reaction of N₂H₃ with NO₂. The slope of the plot of k' versus [NO₂] yielded a value for the observed bimolecular rate coefficient, k_{obs}, which could be fitted to an Arrhenius expression of $(2.36 \pm 0.47) \times 10^{-12} \exp((520 \pm 350)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The errors are 1σ and include estimated uncertainties in the NO₂ concentration.

High-level multi-reference wave function and DFT methods within the MOLPRO utility were explored in this work to gain an understanding of the molecular electronic structures involved in this radical-radical reaction, the efforts of which reveal a new reaction mechanism. It was found that the direct addition of NO₂ to one side of N₂H₃, via a 6-member-ring transition state, forms the N₂H₃NO₂ intermediate, and that addition to the other side of N₂H₃, via a 5-member-ring transition state, forms a complex that undergoes two facile isomerization reactions to form the N₂H₃ONO intermediate, and these intermediates then dissociate to various products. Formation of HONO via direct abstraction was ruled out based on the results of intrinsic reaction coordinate analysis. The rate coefficients for all of the isomerization and dissociation channels were computed via RRKM multi-well master equation simulations of the *E*, *J*-resolved rate coefficients within the VariFlex utility. It was found that the overall reaction follows a radical-radical addition and decomposition mechanism, in which the predominant channel involves the formation of trans-HONO + trans-N₂H₂ at sub-atmospheric conditions. The good agreement with experimental data provides an ability to extrapolate with reasonable confidence the kinetics data to conditions relevant to rocket combustion modeling.

Oral presentations

Thursday, July 26rd, 2018

INELASTIC AND REACTIVE SCATTERING AT GAS-LIQUID INTERFACES

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Abstract

Gas-Liquid interfaces, and the heterogeneous processes that occur at them, are ubiquitous in many important environments, including combustion, atmospheric and biological systems. However, they have been the subject of much less experimental and theoretical study than the gas-phase or gas-solid interface. Relatively little is known about the structure of liquid surfaces, and the interplay between the surface structure and the elementary chemical processes resulting from gas-liquid interaction. In recent years, new experimental techniques and theoretical methodologies have begun to provide detailed understanding in this area.

We have developed a range of molecular beam and spectroscopic methods to study elementary inelastic and reactive scattering processes at the surfaces of liquids in high vacuum. I will focus on the reactive and inelastic scattering of OH at both inert liquid surfaces, and at saturated and functionalised hydrocarbon surfaces that act as models for the surfaces of atmospheric aerosols. Continuously refreshed liquid surfaces are generated by rotating a wheel through a liquid bath. OH radicals are generated in the gas-phase in a molecular beam by pulsed DC electric discharge, and directed at the liquid surface with well-defined velocities and internal state distributions. The OH products of inelastic or reactive scattering, which recoil from the surface into the gas-phase, are probed spectroscopically by LIF, revealing their internal energy distributions. Direct comparison of overall LIF signal between different liquids provides information on sticking co-efficients and relative reactivities. In a new development, LIF real-space imaging of the scattering plane is used to provide information on the OH velocity distributions, for specific final OH rotational states. Together, these measurements provide a comprehensive picture of the elementary processes involved in OH interaction with liquid hydrocarbon surfaces.

GAS-PHASE RADICAL REACTIONS WITH HYDROCARBONS AND AMINES PROBED BY MULTIPLEXED SYNCHROTRON VUV PHOTOIONIZATION MASS SPECTROMETRY

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Abstract

In a variety of complex environments such as combustion, planetary atmospheres and in the interstellar medium, small free radicals play a crucial role due to their high chemical reactivity. Generally, this is demonstrated by their rapid reaction rates and absence of energy barrier when reacting with abundant (un-)saturated molecules. These reactions propagate radical chemistry leading potentially to the formation of larger molecules and are therefore important to better understand and predict molecular growth. Improving the accuracy of chemical models trying to reproduce the chemistry of such environments requires however, quantitative measurements of elementary reactions such as rate coefficients or branching ratios which can be temperature and pressure dependent. Estimating experimentally or theoretically the proportion of exit channels involving reactive intermediates in trace amount is a real challenge. This is highlighted by the few results over a narrow pressure and temperature range available in the literature.

In this work, we probed the products of elementary reactions between C(3P) atoms, with unsaturated hydrocarbons (C₂H₄, C₃H₆, cis-C₄H₈, trans-C₄H₈, iso-C₄H₈) and methylidyne CH with NH₃, NH(CH₃)₂, N(CH₃)₃. The reaction mechanisms involving carbon atoms are important to better understand and predict the growth of carbon containing molecules, including the formation of polycyclic aromatic hydrocarbons (PAHs) in carbon-rich environments. Whereas the methylidyne reactivity with amines brings knowledge about issue of conversion of fuel-nitrogen for combustion.

We used the synchrotron radiation at the Advanced Light Source (LBNL – CA/USA) to probe the products. The chemical reactions were initiated by excimer laser photolysis and the detection performed by coupling the synchrotron-generated tunable VUV light source with a time-of-flight mass spectrometer. The experiments provide kinetic traces and photoionization spectra of the species which is used to determine primary products and isomer distributions leading to fundamental information about the molecular growth mechanisms in different field of research such as combustion or interstellar chemistry.

KINETIC ISOTOPE EFFECT IN THE REACTIONS OF OH AND O(¹D) WITH ISOTOPOLOGUES OF METHANE

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Abstract

Isotopologue abundances are important in studies of the greenhouse gas methane in Earth's atmosphere. There are inconsistencies, however, between modeled and observed ¹³C abundances in the upper troposphere and lower stratosphere, leading to speculation of alternate oxidation pathways. Recent observations of methane in the Martian atmosphere have also stimulated interest in the chemistry of methane under Martian conditions (temperatures down to 170K). Observations of methane isotopologue distributions by missions such as the European Trace Gas Orbiter may eventually provide important clues to the sources and sinks of methane on Mars.

In modeling methane isotope distributions, it is vital to know accurately the kinetic isotope effect (KIE) in the key atmospheric reactions that oxidize methane, especially those of O(¹D) and OH with substitute methane. Such KIEs also provide critical tests of reaction rate theory. Recently, there have been a number of calculations that use path integral formulations to compute quantum mechanical tunneling effects more rigorously in reactions of methane. Previous studies on the KIE of these two oxidation reactions have focused on higher temperature conditions, if at all. Furthermore, these experiments typically required significant methane depletion in static or circulating gas mixtures under constant UV irradiation, conditions that could introduce uncertainties or biases in the measured KIE due to potential secondary chemistry. There is thus a need to measure the KIEs of OH + CH₄ and O(¹D)+CH₄ at lower temperatures and with improved sensitivity.

We present new measurements of the ¹³C and D KIE in the reactions of OH and O(¹D) with singly substituted isotopologues of methane over a wide range of temperatures (155 K and 300 K) relevant to the atmospheres of Earth and Mars. We performed experiments in a temperature-controlled static gas cell reactor and used Frequency-Stabilized Cavity Ring-Down Spectroscopy (FS-CRDS) to measure changes in methane isotope composition. We exploited the significant enhancements in sensitivity of FS-CRDS to investigate reaction conditions with low depletions of methane, thus minimizing errors arising from secondary chemistry. Our measurements are compared with previous experimental and theoretical studies, and suggest a possible resolution to the ¹³C discrepancies observed in Earth's atmosphere.

CROSSED MOLECULAR BEAMS AND THEORETICAL STUDIES OF THE O(³P) + 1,2-BUTADIENE REACTION: PRIMARY PRODUCTS, BRANCHING RATIOS AND INTERSYSTEM CROSSING

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Abstract

The reactions of O(³P) with alkynes, alkenes and dienes play a central role in our understanding of combustion processes and oxidation mechanisms of hydrocarbons. They exhibit many product channels, some of which can only occur via intersystem crossing (ISC) from the triplet to the singlet potential energy surface (PES).^{1,2} Despite extensive studies of their kinetics, little is known about the identity of primary products and the branching ratios (BRs), which are crucially needed to improve combustion models. The most suitable technique to determine unambiguously primary products, the BRs and the detailed dynamics of these reactions is the crossed molecular beams (CMB) method with mass-spectrometric detection and time of flight analysis, empowered with soft ionization by tunable low energy electrons^{1,2} or VUV synchrotron radiation³. The capabilities of this approach have been illustrated in recent, experimental/theoretical studies of the reactions O+ethyne^{1,2}, O+ethene^{1,2}, O+propene^{1,2}, O+allene^{1,2}, O+propyne^{1,2} and O+1-butene⁴, for which product BRs and extent of ISC were quantified.

In this contribution, CMB studies were extended to a reaction with a higher diene: O(³P)+1,2-butadiene, for which little information exists. From product angular and velocity distributions at different mass-to-charge ratios we have identified primary products attributable to **nine competing channels** leading to H displacement, H₂ elimination, and C-C bond breaking pathways forming CO+C₃H₆, HCO+C₃H₅, CH₃CO+C₂H₃, CH₂CHO+C₂H₃, CH₂CO+C₂H₄, H₂CO+C₃H₄, and C₃H₃O+CH₃, determined their BRs and characterized the reaction mechanism. Experimental product BRs and extent of ISC are supported by synergistic RRKM/Master equation non-adiabatic calculations on high-level ab initio triplet/singlet PESs.

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THERMAL DECOMPOSITION OF CH₃I REVISITED: CONSISTENT CALIBRATION OF I-ATOM CONCENTRATIONS BEHIND SHOCK WAVES WITH A DUAL I-/ H-ARAS

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Abstract

For the production of hydrocarbon radicals, R, in shock-tube experiments, the corresponding iodine compounds, RI, are often used as precursors. The comparatively low R-I bond dissociation energies and the low reactivity of I atoms provide favorable conditions for kinetic and mechanistic studies. For a kinetic characterization of the RI decomposition itself, a reliable method for time-resolved detection of I atoms is required. Here, atomic resonant absorption spectroscopy (ARAS) with a microwave discharge as UV-light source is a most useful and well-established technique. A calibration is needed, however, because the Beer-Lambert law is usually not fulfilled in this type of experiments. The calibrations are performed by fitting observed absorbance-time profiles to modeled concentration-time profiles, where the latter have to be obtained from a reliable kinetic mechanism. For calibration of I-atom concentrations, the thermal decomposition mechanism of CH₃I has been used in the past. While CH₃I represents a fairly clean source of I atoms, it is obvious that the resulting calibration curves critically depend on the rate coefficient of the C-I bond fission reaction used in the model. But for the experimental determination of this rate coefficient, a completely independent calibration system is necessary.

In our contribution, we demonstrate that the well-known C₂H₅I pyrolysis can be used for I-atom calibration if I and H atoms are simultaneously monitored at short reaction times with a dual ARAS setup. For verification, we performed extensive studies on the pyrolysis of both C₂H₅I and CH₃I behind reflected shock waves at temperatures between 900 and 1500 K and pressures around 0.4 and 1.7 bar. On the basis of this independent calibration, the rate coefficient for the unimolecular C-I bond-fission reaction in CH₃I could be determined directly from I-atom concentration-time profiles measured in CH₃I pyrolysis experiments. We found that earlier studies probably overestimate this rate coefficient by a factor of two. An updated kinetic mechanism for the CH₃I pyrolysis to calibrate I-atom concentrations in shock-tube/ARAS experiments is presented and discussed.

PRESSURE DEPENDENCE OF CHEMICALLY TERMOLECULAR REACTIONS

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Abstract

The fate of ephemeral complexes formed from bimolecular association reactions, and the phenomenological reactions that result, are determined by the competition between unimolecular dissociation and collisional processes that depend on the surrounding gas mixture. Most mixtures of practical relevance are comprised of multiple components, many of which are reactive, such that these rovibrationally excited intermediates can undergo energy-transferring collisions with multiple different bath gas components as well as reactive collisions. It is well known that the sequence involving energy-transferring collisions that thermalize the complex can be represented within phenomenological kinetic models via termolecular association reactions.

The sequence involving reactive collisions of the ephemeral complex instead results in chemically termolecular reactions, a class of reactions hypothesized in early studies on gas-phase kinetic mechanisms (e.g. Hinshelwood & Williamson 1934) but largely neglected in the present day. Such reactions yield rate laws that are distinct from sequences involving stabilized intermediates. For example, in the regime where collisions of the ephemeral complex are rate-limiting, reactive collisions can serve to increase the overall conversion of bimolecular reactants to products. Recent work has shown that, in environments with high mole fractions of reactive colliders (e.g. premixed flames), these chemically termolecular reactions can be major kinetic pathways and impact global reactivity (Burke & Klippenstein, *Nature Chem.* 2017, 9, 1078).

This talk will highlight recent results from master equation calculations on the effect of pressure on chemically termolecular reactions. We first assess how the kinetics, and rovibrational energy distribution of the complex, transitions from the collision-rate-limited regime (i.e. the low-pressure limit) to the collision-rate-independent regime (i.e. the high-pressure limit). We then explore ways of representing the kinetics of these reactions within rate laws capable of describing pressure dependence in multi-component mixtures (e.g. Burke & Song, *Proc. Combust. Inst.* 2017, 36, 245; Lei & Burke, *Proc. Combust. Inst.* 2018, in review) for their incorporation in phenomenological kinetic models across wide ranges of pressure.

ATMOSPHERIC SIMULATION CHAMBER EXPERIMENTS: BRIDGING THE GAP BETWEEN LABORATORY AND FIELD STUDIES

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Abstract

A large amount of present day knowledge about atmospheric chemistry comes from laboratory studies of elementary chemical reaction kinetics and photochemistry that have been performed in the last decades. The cumulative knowledge has been assembled and is made available to the community in data collections (e.g., by NASA-JPL and IUPAC) providing evaluated data and estimates of uncertainties. Chemical mechanisms of different complexity (e.g., MCM, RACM) attempt to cover the present day knowledge to address specific goals, for example, the prediction of atmospheric OH concentrations, chemical lifetimes and trends of pollutants, the formation of ozone and particulate matter in the troposphere.

It is clear that no chemical mechanism is complete. It may contain simplifications (e.g., lumped species, missing reactions), or contain errors in kinetic data. It is therefore important to test how well models perform as prediction tools. An important test method is the comparison of modelled concentrations of atmospheric compounds with corresponding observations from field experiments. The interpretation of field data, however, can be complicated by not-well defined boundary conditions, local emissions and transport processes, and chemical segregation. Some of these difficulties can be avoided by using atmospheric simulation chambers. They allow complex chemical mechanisms to be tested under largely controlled conditions. In this presentation, an overview will be given of how atmospheric chambers can be used to investigate specific chemical systems, for example the photochemical degradation of biogenic VOCs, that are difficult to access in the field and on a laboratory scale.

A GAS KINETICIST'S LIFE: A REMINISCENCE TO DR. IAN BARNES

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Abstract

On January 1, 2018 our colleague Ian Barnes died unexpectedly aged 66 during his holidays in Belfast, Northern Ireland. Ian Barnes spent more than 40 years at the University of Wuppertal in the Lab for Physical Chemistry after receiving his PhD at the University of Belfast. Ian became quite quickly one of the key persons in the department.

His invaluable contributions to the development of our understanding of atmospheric processes with special emphasis on organic sulphur compounds and aromatic hydrocarbons will be reviewed.

THE PHOTOLYSIS MECHANISM OF MONOAROMATIC RING OPENING PRODUCTS - UNSATURATED 1,4 DICARBONYLS -FROM CHAMBER EXPERIMENTS

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Abstract

Unsaturated 1,4-dicarbonyls are major ring opening products in the photo-oxidation of both monoaromatic compounds (emitted to the atmosphere from fossil fuel burning, solvent evaporation and industrial uses) (Gómez Alvarez et al., ES&T, 41, pp. 8362-8369 (2007)), and furans (a major component of biomass burning emissions) (Gómez Alvarez et al., Atmos. Env., 43, pp. 1603-1612 (2009); Aschmann et al., JPCA, 118, pp. 457-466 (2014)). However, there have been very few studies on the fate of these key intermediate species in the atmosphere.

The photo-oxidation chemistry of unsaturated 1,4-dicarbonyls is one of the major radical sources in the oxidation of monoaromatic compounds in the current Master Chemical Mechanism (MCMv3.3.1; mcm.leeds.ac.uk/MCM). However, there is a limited fundamental understanding of the underlying mechanism of this chemistry. Previous chamber experiments have suggested that there are 'missing' radical sources in current aromatic oxidation schemes (Bloss et al., ACP, 5, pp. 623-639 (2005a)), and these may be linked to these poorly understood intermediates.

Here we report the results from a series of experiments at the outdoor environmental simulation chamber, EUPHORE, Valencia, under a range of atmospherically relevant conditions. We examine the photolysis of (*E*)-butenedial, (*Z*)-4-oxo-pent-2-enal and (*E*)-4-oxo-pent-2-enal under ambient photolytic conditions. These experiments were performed as part of the EXACT and TOXIC campaigns, which were aimed at improving the mechanistic understanding of the oxidation of monoaromatic compounds under atmospheric boundary layer conditions (Bloss et al., ACP, 5, pp. 641-664 (2005b); Pereira et al., ES&T, 49, pp. 13168-13178 (2015)).

Results show that the major fate of these species in the atmosphere is photolysis. The major products of the photolysis of butenedial are the cyclic species 3(H)-furan-2-one, maleic anhydride, acrolein, and CO. There is very low radical production and negligible production of the α -dicarbonyl glyoxal. We propose a mechanism involving an initial γ -hydrogen abstraction leading to a ketene-enol species, which can undergo isomerisation or react further, to account for the observed products.

Comparison of the proposed mechanism to the MCMv3.3.1 shows that the MCM schemes overestimate radical production in unsaturated 1,4 dicarbonyl photolysis.

PRODUCTS AND MECHANISMS FOR THE ATMOSPHERIC OXIDATION OF DIMETHYLBENZOQUINONES

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Abstract

Aromatic hydrocarbons (AH) make an important contribution to the formation of atmospheric photooxidants (30% of total) and are responsible for up to 10% of the global secondary organic aerosol burden from anthropogenic sources [1]. As a result, there has been wealth of studies on the atmospheric reactivity of AHs, with many first generation oxidation products identified. However, the further atmospheric reactions of these first generation oxidation products are considerably less well studied. This study represents new investigations into the gas phase oxidation products formed from the OH radical initiated oxidation of the dimethylbenzoquinone isomers, which are first generation products from the gas phase degradation of the xylenes and/or dimethylphenols [1]. This work builds on our previous study which reported rate coefficients of the order of $10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ for the reaction of these compounds with OH radicals [2].

The product studies were performed in a 3.9 m³ atmospheric simulation chamber (Cork, Ireland) using *in situ* FTIR (Fourier Transform Infrared) spectroscopy and *off-line* GC-MS (gas chromatography–mass spectrometry) after derivatization with PFBHA (O-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine). Additional studies have been performed in a 1080 L quartz glass reactor (Wuppertal, Germany) using *in situ* FTIR and on-line PTR-TOF-MS (Proton Transfer Reaction –Time of Flight – Mass Spectrometry). A new mechanism is proposed for the formation of 4-methyl-2,3,6-trioxo-4-heptenal, 2-oxopropanedial and 2,3,4-trioxopentane, along with methylglyoxal and glyoxal, from the reaction of 2,6-dimethylbenzoquinone with OH radicals. A similar mechanism is proposed in the reaction of 2,5-dimethylbenzoquinone reaction with OH radicals to produce 5-methyl-2,3,6-trioxo-4-heptenal, 2,3-dioxobutanal, methylglyoxal and glyoxal. Atmospheric implications of the work are also discussed.

Acknowledgements

EUROCHAMP-2020 Infrastructure Activity is gratefully acknowledged. Support provided by UEFISCDI within the PN-III-P2-2.1-PED2016-1621 and PN-III-P4-ID-PCE2016-0807 projects is gratefully acknowledged.

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REACTIVITY OF γ -TERPINENE AND α -TERPINENE WITH NO₃ RADICAL: A COMPARATIVE KINETIC AND MECHANISTIC STUDY.

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Abstract

Biogenic Volatile Organic Compounds (BVOCs) are highly emitted by vegetation and play a key role in atmospheric chemistry [R. Atkinson et J. Arey, *Atmos. Env.* 37 Supplement No. 2, pp. S197-S219 (2003)]. They are very reactive with atmospheric oxidants (OH, NO₃, O₃) and significantly contribute to the formation of Secondary Organic Aerosol (SOA) at the global scale [S. S. Brown and J. Stutz, *Chem. Soc. Rev.* 41, pp. 6405–6447 (2012)]. In addition, night-time chemistry initiated by NO₃ radicals leads to the formation of Organic Nitrates (ON) which behave as reservoirs for reactive Nitrogen. However, the reactivity of NO₃ radical with BVOCs other than isoprene and α - and β -pinene, remains poorly understood.

γ - and α -terpinene are among the most common monoterpenes [C. Geron et al., *Atm. Env.* 34, pp. 1761-1781 (2000)] but have been subject to few experimental studies. These compounds have very similar structures which differ only by the conjugated or not conjugated C=C bonds. As expected, this difference has been shown to significantly affect the rate of the reaction. However, very little is known about chemical mechanisms and the SOA formation.

The aim of this work is to study the reactivity of these two BVOCs with NO₃ radical, and to determine the influence of double bounds positions on the reactivity. Chambers experiments were conducted to investigate the kinetic and the mechanism of these reactions, and to calculate SOA and ON formation yields. Two simulation chambers at LISA were used: CSA chamber, a 1 m³ Pyrex reactor [J.-F. Doussin et al., *Analisis.* 25, pp. 236-242 (1997)] and CESAM chamber (<http://cesam.cnrs.fr>), a 4 m³ stainless steel reactor [J. Wang et al., *Atmos. Measur. Tech.* 4, pp. 2465-2494 (2011)], dedicated to multiphasic process studies. They are equipped with a large panel of analytical techniques for the characterization of both gaseous (FTIR, PTR-ToF-MS, IBB-CEAS, NO_x and O₃ analyzers) and condensed phases (SMPS and filter sampling).

Kinetic (by absolute and relative determinations) and mechanistic results are presented and discussed. In particular, very different SOA yields have been observed for the two compounds. Explanations and mechanisms are proposed in regard to differences in the chemical structure and detected products.

KINETIC STUDY OF THE CH₃O₂ + HO₂ CROSS-REACTION IN THE HIGHLY INSTRUMENTED REACTOR FOR ATMOSPHERIC CHEMISTRY

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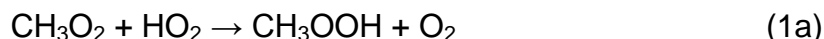
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Abstract

Peroxy (RO₂) radicals are highly reactive species critical in most atmospheric oxidation. They are formed in the degradation of volatile organic compounds (VOCs) and can lead to the formation of O₃ and aerosols in the atmosphere, making them central molecules to understand. The most abundant RO₂ radical in the atmosphere is predicted to be methylperoxy (CH₃O₂) however its concentration has not yet been measured. Under high NO_x conditions (e.g. in urban areas) the daytime chemistry of CH₃O₂ is dominated by reaction with NO. However, under low NO_x conditions (e.g. in remote areas) the daytime chemistry of CH₃O₂ is dominated by its self-reaction and the reaction with HO₂ or other RO₂ radicals present. In this study we focus on the reaction of CH₃O₂ with HO₂ that follows two pathways:



Given the intermediate nature of RO₂ radicals, direct detection is challenging. The current IUPAC recommended value for the reaction rate coefficient is associated with a ~40 % uncertainty mainly from the use of UV spectroscopy in the previous studies of this reaction (R. Atkinson, et al., ACP, 6, p. 3625-4055 (2006); IUPAC 2009: <http://iupac.pole-ether.fr/>). A more selective and sensitive method is used in this study adapted from laser induced fluorescence spectroscopy; fluorescence assay by gas expansion (FAGE). It is used to detect CH₃O₂ radicals as well as HO₂ radicals within the highly instrumented reactor for atmospheric chemistry (HIRAC) (D.R. Glowacki et al., ACP, 7, p. 5371-5390 (2007); D.E. Heard and M.J. Pilling, Chem.Rev., 103, p. 5163-5198 (2003); L. Onel et al., AMT, 10, p. 3985-4000 (2017)) by their conversion to CH₃O and OH, respectively, in the excess of NO. Subsequently CH₃O and OH are detected by FAGE with laser excitations at ca. 298 and 308 nm, respectively.

In HIRAC, experiments were performed to investigate the overall rate of reaction (1) using a mixture containing CH₄, CH₃OH, and Cl₂ in 1 bar of synthetic air at varying temperatures. The radicals were formed following the photolysis of Cl₂ and Cl-initiated H atom abstractions from CH₄ and CH₃OH followed by reactions with O₂. The second order decays for the two radicals were used to obtain kinetic data of reaction (1) showing a negative temperature dependence. The preliminary results are in good agreement with IUPAC values.

Cl ATOM INITIATED PHOTO-OXIDATION REACTION KINETICS OF METHYL AND ETHYL PROPIONATE

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Abstract

Esters are volatile oxygenated organic compounds that are emitted into the atmosphere from biogenic and anthropogenic sources (F. Cavalli et al., J. Phys.Chem. A , 104, pp. 11310 - 11319 (2000)). Esters are used as industrial solvents and as reagents during the manufacture of perfumes and food flavoring (F. Billaud., J. Am.Oil Chem. Soc., 72, pp. 1149–1154, (1995)). Esters are emitted into the atmosphere from natural sources (i.e., vegetation) and are also formed in the atmosphere as oxidation products of ethers used as automotive fuel additives (Bendtz,K.; Oilseeds and products: Biofuels situation in the European Union 2005, GAIN report; USDA and Foreign Agricultural Service: Washington DC, (2007)). Moreover, methyl propionate, ethyl propionate and the corresponding radicals produced in the reaction of Cl atom/ OH radical were observed to be important intermediates in the pyrolysis of biodiesel.

In the present study, the gas phase kinetics of methyl propionate and ethyl propionate with Cl atoms were measured as a function of temperature (263-363 K) at pressure ~760 Torr using the relative rate technique. The product analysis was performed by using GC-MS and GC-FTIR. The temperature dependent rate coefficient obtained are k_{MP+Cl} (263-363K) = $[(3.25 \pm 1.23) \times 10^{-16}] T^2 \exp [-(33 \pm 4)/T]$ $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ and k_{EP+Cl} (263-363K) $[(6.58 \pm 1.92) \times 10^{-24}] T^{4.5} \exp [(1124 \pm 90)/T]$ $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$. Theoretical calculations were also performed using variational transition state theory (VTST) with small curvature tunneling (SCT) and the kinetic data were obtained over the temperature range of 200-400 K using CCSD(T)/cc-pVDZ in combination with B3LYP/6-31+g(d,p) and BHandHLYP/6-31+g(d,p) level of theory. The branching ratios, thermochemistry, atmospheric implications, absorption cross-section and degradation path ways of methyl propionate and ethyl propionate were also studied. The detailed studies of the title reaction will be presented in the conference.

ISOMERIZATION AND DECOMPOSITION OF ISOPRENE'S DELTA-(Z)-HYDROXYPEROXYL RADICALS

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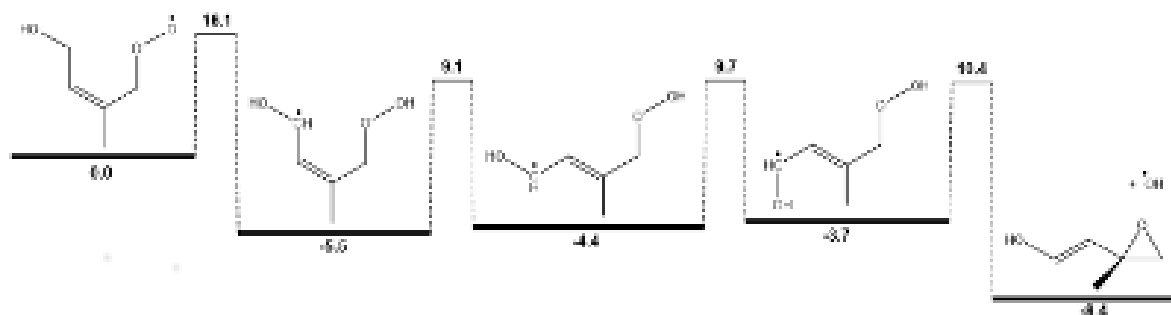
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Abstract

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 degradation pathways are not yet fully understood.

In the troposphere isoprene reacts rapidly with OH and then O₂ to produce a suite of hydroxyperoxyl radicals (ISOPO₂), incorporating beta-OH and *E* or *Z* delta-OH functionality. It has been shown that the delta-(*Z*)-ISOPO₂ radicals can undergo a facile intramolecular hydrogen shift to produce an alpha-hydroxyalkyl radical intermediate which can react with O₂ to yield hydroperoxy aldehydes (HPALDs).

This study uses computational chemistry calculations to demonstrate that the delta-(*Z*)-ISOPO₂ radicals undergo further rearrangements, with lower barriers, leading to direct OH radical reformation along with an epoxide (See Figure, energies in kcal/mol). RRKM theory / master equation simulations are used to predict OH radical reformation yields vs intermediate stabilization, and suggest that OH reformation will compete with HPALD production in the troposphere.



ATMOSPHERIC AUTOXIDATION IS INCREASINGLY IMPORTANT IN URBAN AND SUBURBAN NORTH AMERICA

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Abstract

Biogenic emissions of volatile organic compounds have been shown to contribute to the formation and growth of secondary organic aerosols, through autoxidation (T. Berndt et al. Nature Comm., 7, 13677 (2016)). Autoxidation is a process where a peroxy radical, formed by e.g. reaction with OH and then addition of O₂, abstracts a hydrogen from another place in the molecule (often referred to as hydrogen shift reactions or H-shifts). This leads to a new alkyl radical carbon atom, to which another O₂ molecule can add. An example is shown in the figure. Autoxidation is a way to form highly oxygenated molecules, which are likely to partition into the particle phase.

Autoxidation is often considered primarily in unpolluted environments, where low concentrations of NO_x lead to slow bimolecular reactions and enhances its importance. In this study we show autoxidation to be important for a compound derived from gasoline vehicle emissions, 2-hexanol, even in urban areas in North America (Praske et al. PNAS, 115, pp. 64-69 (2018)). Using both theoretical and experimental techniques, we have determined the rate of autoxidation of 2-hexanol derived peroxy radicals. Because of tighter emission standards, NO_x levels in cities across North America have decreased and are now at a level where autoxidation is becoming important for atmospheric oxidation chemistry.

Polanyi Lecture

MULTIPHASE CHEMISTRY IN THE ATMOSPHERE: IT ALL STARTS WITH GASES

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Abstract

Gas phase dynamics, kinetics and mechanisms has a long and storied history, providing unparalleled insights into reactions at the atomic and molecular level. The field of atmospheric chemistry was largely founded on such understanding of gas phase reactions. Over the years, our ability to measure gases at smaller and smaller concentrations has revealed that many species that might previously have been considered essentially involatile are, in fact, present at sub-part-per-trillion (ppt) levels. In the case of organics, these can be formed by oxidation in the gas phase of larger species such as biogenics. They are believed to serve as nuclei for particle formation, and subsequently contribute to particle growth. Thus, gas to particle conversion represents a continuum from the gas phase to very low volatility particles, i.e., multi-phase systems. The author will describe her journey from having her interest in atmospheric chemistry sparked by the chemistry of the aurora borealis through to studies of atmospheric gas phase kinetics and mechanisms and more recently, multi-phase systems. In the end "it all starts with gases!".

Posters

1. REACTION KINETICS FOR THE UNIMOLECULAR DECOMPOSITION OF C₅ AND C₆ CYCLIC KETONES

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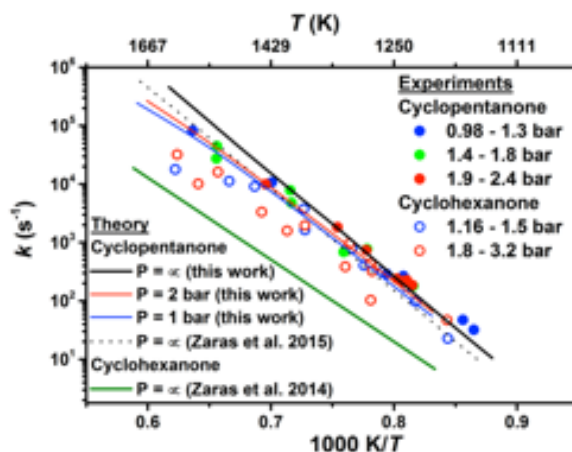
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Abstract

The thermal decomposition of cyclopentanone and cyclohexanone was studied behind reflected shock waves over a wide range of experimental conditions ($T = 1150 - 1600$ K, $P = 1 - 3.2$ bar). We followed the reaction kinetics by monitoring CO formation for cyclopentanone decomposition using quantum cascade laser operating near $4.56 \mu\text{m}$, while we used HeNe laser to follow the decay of cyclohexanone near $3.39 \mu\text{m}$. Our results show that cyclopentanone exclusively decomposes to produce CO and C₂H₄ under our experimental conditions. The experimental results are well complemented by our ab initio/master equation calculations.

Interestingly, cyclohexanone exhibited similar reactivity at the low-temperatures end of our experiments but deviated significantly at higher temperatures as compared to cyclopentanone decomposition. Our experiments clearly showed that cyclohexanone undergoes decomposition via different reaction mechanism compared to cyclopentanone, and that cyclohexanone would require a lower barrier to overcome than that of cyclopentanone. The fact that we did not obtain CO yield of ~ 1 at high temperatures for cyclohexanone may point that the reaction mechanism by which C₅ and C₆ cyclic ketones decompose are different. This observation resonates well with a recent theoretical work from Zaras et al. (A. Zaras, IJCK, 47, pp. 439-446 (2015)). We find good agreement between our experimental data and theoretical results for cyclopentanone decomposition. However, this is not the case for cyclohexanone.



2. DETERMINATION OF THE HOOCH₂OCH₂ (QOOH) + O₂ RATE COEFFICIENT UNDER PROPAGATING / BRANCHING CONDITIONS

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Abstract

In combustion, autoignition is a consequence of explosive chain branching. In the low-temperature regime (<1000 K) autoignition is the consequence of a series of reactions initiated by the reaction of the hydroxyl radical (OH) with the fuel (RH):



Recently, there have been absolute determinations of k_4 via either direct detection of QOOH [J. D. Savee et al., Science 347 (2015)] or via directly following the QOOH decomposition product.[J. Zador et al., Physical Chemistry Chemical Physics 15 (2013)] The measured k_4 were slow. However, these QOOH do not lead to propagation/branching so these measured rate coefficients, k_4 , might be unrepresentative of k_4 for QOOH that do lead to branching.

k_1 can be determined in straightforward experiments where OH is measured in the presence of varying [RH] (ether) over a range of temperatures. If small amounts of [O₂] are then added to the system, over a range of temperatures and pressures, then k_2 and k_3 can be determined by measuring the recycled OH via:



If [O₂] is high, then propagation/branching is observed for both dimethyl/diethyl ether. At lower T, < 600 K, the recycled OH is just k_4 , where the recycled OH transitions from k_6 to k_4 as [O₂] is increased, $k_4 > k_6$: Experimental data and its analysis will be presented that shows how k_1 , k_2 , k_3 , k_4 , and k_6 are determined. Sophisticated direct multi-trace analysis to the above scheme is the key to determining the rate coefficients of the system, where the R + O₂ reaction is described by its Master Equation, MESMER. The analysis determined k_4 for HOOCH₂OCH₂ (QOOH) + O₂ to be fast, $> 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, which is much faster than for non-branching QOOH. Above 600 K, chain branching is evident in the data; the analysis of this data is ongoing.

Experimental data and its analysis will be presented that shows how k_1 , k_2 , k_3 , k_4 , and k_6 are determined. Sophisticated direct multi-trace analysis to the above scheme is the key to determining the rate coefficients of the system, where the R + O₂ reaction is described by its Master Equation, MESMER. The analysis determined k_4 for HOOCH₂OCH₂ (QOOH) + O₂ to be fast, $> 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, which is much faster than for non-branching QOOH. Above 600 K, chain branching is evident in the data; the analysis of this data is ongoing.

3. COMPUTATIONAL STUDY OF α -ACROLEIN RADICAL ASSOCIATION REACTIONS WITH $^3\text{O}_2$, THERMOCHEMISTRY AND KINETICS

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Abstract

Acrolein, α , β -unsaturated (acrylic) aldehyde, is one of the simplest multifunctional molecules, containing both an alkene and an aldehyde group. Acrolein is an atmospheric pollutant formed from the photochemical oxidation of the anthropogenic VOC 1,3-butadiene, and from polymer degradation. It also serves as a model compound for methacrolein (MACR) and methyl vinyl ketone (MVK), in modeling and understanding the oxidation products of the biogenic VOC isoprene. Acrolein is also a product from biological and numerous combustion oxidation processes. A new lower energy conformer (electronic structure) of the secondary acrolein vinyl radical ($\text{CH}_2=\text{C}\cdot\text{-CHO}$) with a linear structure, compared to the common bent structure, has been identified by our calculations related to the thermochemistry this α -acrolein vinyl radical. The association reaction of α -acrolein radical with molecular oxygen to form a peroxy radical which further reacts via a number of low energy channels including to chain branching forming an alkoxy radical plus oxygen. The well-depth is determined as 53 kcal mol^{-1} for α -acrolein radical association with $^3\text{O}_2$. Chain branching of the $\text{R}\cdot + \text{O}_2$ to $\text{RO}\cdot + \text{O}$ is an important reaction pathway in this structure α -acrolein radical oxidation.

4. CROSSED BEAM STUDIES OF THE O(³P) REACTION DYNAMICS WITH BENZENE AND TOLUENE: PRIMARY PRODUCTS AND BRANCHING RATIOS

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Abstract

Reactions of O(³P) with benzene and toluene are of interest for modeling of aromatic oxidation. To improve current kinetic models knowledge of primary products and branching ratios (BRs) is needed. For O(³P)+C₆H₆ energetically allowed products are phenoxy+H and cyclopentadiene+CO, with the latter involving intersystem crossing from triplet to singlet potential energy surfaces. Despite extensive kinetic¹, dynamical² and theoretical^{1,3} studies the BR of CO formation under single-collision conditions remains an open key question. Moreover, little is known about the BRs for O(³P)+toluene. Previous crossed molecular beam (CMB) studies² and theoretical calculations³ indicated that O(³P)+C₆H₆ leads to C₆H₅O+H, with C₅H₆+CO ≤5%. However, recent kinetic studies¹ (300-1000 K; 1-10 Torr) by synchrotron photoionization mass spectrometry (MS) detected phenol, C₆H₅O+H, and C₅H₆+CO products with BRs at 900 K and 4 torr of 0.33 for each of the 3 channels, which differ significantly from previous work^{2,3}.

Recently, we have shown that the CMB technique with soft electron ionization MS detection permits to identify all primary products and determine the BRs for multichannel O(³P) reactions with unsaturated hydrocarbons (ethyne, ethene, propene, allene, propyne, 1-butene)⁴. Here, we extend CMB studies to O(³P,¹D) reactions with the aromatic prototypes benzene and toluene. For O(³P)+benzene we find phenoxy as main product and CO minor. For O(¹D)+benzene we find as dominant products CO+H+C₅H₅(cyclopentadienyl), with CO+C₅H₆ and C₆H₅O+H being smaller, thus confirming previous CMB results⁵. For O(³P)+toluene main channel is phenoxy+CH₃ followed by methylphenoxy+H, and no CO. For O(¹D)+toluene dominant channel is also phenoxy+CH₃, with methylphenoxy+H and CO+methylcyclopentadiene also formed.

Acknowledgments: Financial support by "Fondazione Cassa Risparmio Perugia" (Project Code 2015.0331.021 Scientific & Technological Research) and COST Action CM1404 SMARTCATs is acknowledged.

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5. THEORETICAL INVESTIGATION OF THE KINETICS OF LOW-TEMPERATURE COMBUSTION CHEMISTRY OF PROPYLBENZENE

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Abstract

Numerical kinetic modeling of combustion behaviour of fuel is an important, although, challenging task especially at low temperatures and high pressures [1]. Therefore, combustion community develops gas-phase detailed models to simulate low-temperature autoignition and oxidation of the components (alkanes, cycloalkanes, & aromatics) of diesel and gasoline fuels to understand their combustion mechanism [1]. Propylbenzene is one of the component of real fuels and being tested as a candidate for its application in HCCI engines [2]. Low-temperature peroxy chemistry of propylbenzene has not been investigated in details in spite of lots of experimental and modeling investigations on alkyl-substituted aromatic fuels [2]. Thus, detailed potential energy surface of the reactions of propyl-benzyl radicals with O₂ were calculated at B3LYP/aug-cc-pVTZ level of theory and refined at the CCSD(T)/cc-pV ∞ Z//UM06-2X/Aug-cc-pVTZ levels. We utilized the Gaussian 09 suite of programs for quantum chemical calculations [3]. High-pressure limit rate constants of all oxidation reaction channels were evaluated using transition state theory. Variational transition state theory combined with CASPT2(7e,5o)/cc-pVTZ//UB3LYP/Aug-cc-pVTZ level of quantum chemical method were utilized for the rate constants calculations of barrierless entrance channels involving radical additions with O₂. High-level ab initio results were employed in RRKM analysis coupled with steady-state master equation analysis with single exponential down model for collisional energy transfer probability and collision frequency using Lennard-Jones model (L-J model) to calculate $k(T, P)$ of chemical activation reactions in the 300-2500 K temperature and 0.1-100 atm pressure range. Finally, we have refined a detailed kinetic model of propylbenzene available in the literature [4] and optimized based on the combustion kinetics of low temperature peroxy chemistry evaluated from present theoretical and computational analysis. Our results suggest that high pressure rate coefficients are sufficient enough under most of combustion conditions.

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6. EXPERIMENTAL AND NUMERICAL KINETIC STUDY OF THE OXIDATION OF C₅H₁₀O₂ ESTERS ISOMERS

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Abstract

Biodiesel is considered as an interesting alternative to petroleum derived Diesel fuel in order to mitigate the increasing demand on oil products for transportation. It also offers an opportunity to limit the emissions of carbon dioxide in the atmosphere by a short carbon cycle from the carbon dioxide emitted during the combustion of the plant by-products to the use of this CO₂ for the plant to grow. Indeed, biodiesel is composed of monoalkyl esters of long carbon chain fatty acids obtained from the transesterification of renewable lipid feedstock with mostly methanol, but also ethanol or higher molecular weight alcohols. Therefore, esters have been the subject of several studies since the beginning of the 21st century. Starting with the pioneer work on methylbutanoate (Fisher et al. 2000), recent studies focused on esters with longer acid chains (Herbinet et al. 2008), unsaturations (Zhang et al. 2014) or longer alcohol chains (Dayma et al. 2012).

In this work, we report experiments and modeling on a series of four esters with five carbon atoms (C₅H₁₀O₂), namely, methylbutanoate, ethylpropanoate, propylacetate, and butylformate. The oxidation of these esters was performed in a jet-stirred reactor under the same experimental conditions ($\tau = 700$ ms, $p = 10$ atm, same equivalence ratios and initial fuel mole fractions). The mole fraction profiles obtained from these experiments were used to develop a unique detailed kinetic mechanism for the oxidation of these four esters, which performs well against our experimental data and data from the literature. Although, these esters are isomers, this work highlighted the influence of the position of the ester function in terms of global reactivity and distribution products. In particular, this comparison shows the importance of molecular reactions during the oxidation process of these esters. However, efforts are still needed to improve our understanding of the influence of the ester function on H-abstraction reactions.

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7. EXPERIMENTAL STUDY OF ATMOSPHERIC LAMINAR PREMIXED $\text{CH}_4/\text{O}_2/\text{N}_2$ AND $\text{CH}_4/\text{H}_2/\text{O}_2/\text{N}_2$ FLAMES IN SOOTING CONDITIONS

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Abstract

Experimental investigation of the chemical structure of methane flames with and without different portion of hydrogen have been performed. Various stable species mole fraction have been measured by gas chromatography in 27 premixed laminar flames operating at equivalence ratios ($1.6 < \Phi < 1.9$) close to the “nucleation flame” conditions. The methane nucleation flame has been identified by incandescence technique (LII) at $\Phi = 1.82$. The approach and the definition of “nucleation flame” have been previously reported in our recent work [1], [2].

The experimental results showed that hydrogen addition (lower than 2% in the total flow) as reactants affects only benzene mole fraction. At a fixed C/O ratio, a reduction of the benzene peak mole fraction (20%) is observed whereas its formation proceeds close to the burner surface. Similar investigations carried out by replacing hydrogen by helium allowed to exclude the diluted effect of hydrogen in our studied flames. However the addition of the same quantity of hydrogen (1.85% in the total flow) enhanced (50%) benzene peak mole fraction and its mole fraction in the post flame region. Under these conditions, a more intensive yellow color characteristic of the soot emission has been visually observed. Similar experimental conclusions have been drawn in our previous work conducted in natural gas flames under lean conditions [3].

The impact of hydrogen on some selected PAHs, soot volume fraction and particle size distribution (PSD) is in progress. The results should confirm a key role of benzene in soot formation and the importance of H atoms in their chemical growth process.

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8. ON THE AUTO-IGNITION KINETICS OF AMMONIA AT LOW TEMPERATURES AND HIGH PRESSURES

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Abstract

Ammonia is currently being discussed as a potential fuel for applications in gas turbines and gas engines, due to its low reactivity and relatively good energy density (22.5 MJ/kg). It is a carbon-free energy carrier which can be produced with renewable sources such as wind and solar energy using P2X technology.

However, for its future use as fuel, its ignition and combustion characteristics need to be well understood and the reaction kinetics of its oxidation well investigated. A major part of the previous research has focused on the ammonia oxidation at high temperatures and low pressures, while ignition measurements for pure ammonia or ammonia blended with other gaseous fuels (such as hydrogen or methane) at high pressures and low-to-intermediate temperature is rare.

In this study, autoignition of NH_3/O_2 and $\text{NH}_3/\text{H}_2/\text{O}_2$ mixtures has been studied in a Rapid Compression Machine (RCM) at pressures between 20 and 60 bar, temperatures from 950 to 1150 K, and equivalence ratios from 0.5 to 2. The effect of hydrogen-ammonia ratio in fuel has been also investigated. It is observed in the experiments that a higher H_2 mole fraction in fuel improves the reactivity of the mixture. With 20% H_2 in fuel, richer mixtures have shorter ignition delay times. With 5% H_2 in fuel, the stoichiometric mixture presents the shortest ignition delay time. In the mixtures without hydrogen, leaner mixtures show higher reactivity. Detailed chemical kinetic modeling is performed using the Cantera code by introducing a wall velocity profile into the constant volume reactor to compensate for the heat loss during and after compression in RCM. Modeling with the reaction mechanism from Klippenstein et al. [1] predicts the ignition delay time well for fuel-lean or stoichiometric mixture at higher pressure. At lower pressure or for rich mixtures the model underestimates the ignition delay time. Kinetic analysis further demonstrates that the two channels of the reaction $\text{NH}_2 + \text{NO}$ are dominant for the ammonia auto-ignition in the investigated temperature range, and the reactions involving H_2O_2 are important for ammonia-hydrogen blends.

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9. A HIGH TEMPERATURE EXPERIMENTAL INVESTIGATION OF ALLYL SELF-REACTION AND ALLYL + OH

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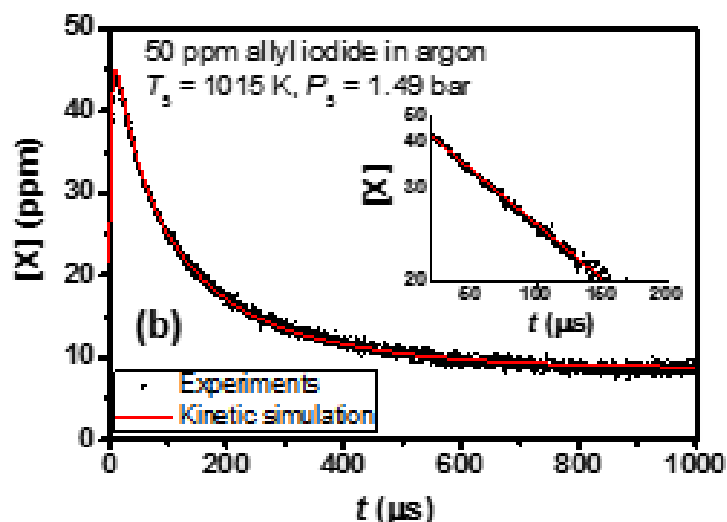
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Abstract

Resonantly stabilized hydrocarbon radicals, such as allyl (C_3H_5), play a crucial role in combustion processes. Allyl has a resonance energy of ~ 61 kJ/mol and being thermodynamically stable, it exhibits slow reactivity towards molecular oxygen. It can, therefore, build up to high concentrations making radical-radical reactions its major loss pathways under combustion conditions. In this work, we have investigated the self-reaction of allyl radicals and its cross-reaction with hydroxyl radical by employing shock tube and laser absorption techniques. We carried out experiments behind reflected shock waves over the temperature range of 800 – 1200 K and pressures of 1.1 – 2.5 bar. We generated allyl and OH radicals thermally by using allyl iodide (C_3H_5I) and tert-butyl hydroperoxide (TBHP) as radical precursors, respectively. We monitored OH near 306.69 nm and C_3H_5 near 220 nm using UV laser absorption to follow the reaction kinetics.

Self-recombination reaction of allyl radicals showed a small negative temperature dependence, but no noticeable fall-off behavior over 1.15 – 1.96 bar, giving a mean value of $k(C_3H_5+C_3H_5) = (1.0 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Likewise, the cross-reaction of allyl and OH radicals did not exhibit discernible pressure and temperature dependence under our experimental conditions, indicating a barrierless addition of OH to allyl yielding C_3H_5OH , and the measured rate coefficients can be represented by an average value of $k(C_3H_5+OH) = (9.3 \pm 0.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.



10. FORMATION STUDY OF NO₂ AND NO IN METHANE OXIDATION IN FLOW TUBE AT HIGH TEMPERATURE (UP TO 1973 K)

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Abstract

The experimental study of the oxidation of methane was carried out in a novel apparatus developed to investigate the formation of NO and NO₂ at high temperature. This apparatus is composed of a flow tube reactor made of alumina to resist to high temperatures, and of a tubular oven (provided by Carbolite Gero) working over a wide range of temperatures up to a maximum of 2073 K. The reactor inside diameter is about 4 mm and the residence time around 30 ms. The inlet concentration of methane was set to a small value of 1000 ppm to minimize the heat release from the reaction and to help maintaining the reaction temperature constant in the central zone of the tubular reactor. Experiments were carried out at three equivalence ratios to cover rich ($\varphi = 1.25$), stoichiometric and lean conditions ($\varphi = 0.4$). The carrier gas was nitrogen. Experiments were performed at a pressure slightly above the atmospheric pressure and over the temperature range 1573 – 1973 K. Temperature profiles along the tubular reactor have been measured using a R-type thermocouple. This temperature profile is needed to run simulations under accurate conditions. Especially at such high temperatures, the reaction product composition can be strongly influenced by the temperature profile at the outlet of the reactor. Two different diagnostics were used for the detection of species: gas chromatography (GC), and chemiluminescence NO_x analyzer. The NO_x analyzer was used for the quantification of NO and NO₂. Reaction products were directly sampled at the outlet of the reactor using transfer lines. Under these conditions, the fuel is totally consumed under all equivalence ratio. This last parameter has a strong influence on the distribution of reaction products. As far as NO_x as concerned, no NO₂ was detected under the conditions of this study, which is not surprising given the high temperature of these experiments. NO formation was observed from 1625 K with a progressive increase of the mole fractions with temperature under the three studied equivalence ratios. Larger mole fractions of NO were observed under rich conditions (14 ppm at 1973 K), followed by the stoichiometric case (12 ppm at 1973 K) and then the leaner one (5 ppm at 1973 K).

The work leading to this intervention has received funding from the European Union Horizon H2020 Programme (H2020-SPIRE-04-2016) under grant agreement n°723706

11. NO₂ FORMATION IN THE COMBUSTION OF N-HEPTANE: KINETIC MODELING AND COMPARISON TO ENGINE MEASUREMENTS WITH DIESEL FUEL

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Abstract

In recent years, the reduction of nitrogen oxides emissions has been a focus in engine development because of stricter regulations in emission standards. To comply with the limits, various exhaust after treatment methods have been developed such as selective catalytic reduction (SCR) and NO_x storage catalysts (NSC). High NO₂/NO ratios lead to increased efficiencies of the SCR, a reason why oxidation catalysts are used to oxidize NO to NO₂.

Another possibility for increasing the NO₂/NO ratio is internal engine measures. In our study, several parameters were varied at a single-cylinder diesel engine and the effects on the formed amounts of NO and NO₂ as well as on the NO₂/NO ratio were investigated (M. Rößler et al., SAE Int. J. Engines, 10, pp. 1880 – 1893 (2017)). In order to better understand the influences found, chemical kinetic simulations were performed. To this end, a reaction-kinetic model was developed that describes the n-heptane combustion in air and the associated nitrogen oxide formation. Here, n-heptane was selected as a model fuel because it has similar autoignition properties as diesel fuel. The mechanism consists of a n-heptane oxidation mechanism taken from Mehl et al. (M. Mehl et al., Proc. Combust. Inst., 33, pp. 193 – 200 (2011)) and a NO_x submechanism that was adopted from a work by Faravelli et al. (T. Faravelli et al., Combust. Flame, 132, pp. 188 – 207 (2003)) and supplemented by coupling reactions mainly according to Glaude et al. (P.A. Glaude et al., Energy Fuels, 19, pp. 1839 – 1849 (2005)). The NO_x submechanism (35 species and 1176 reactions) was reduced for diesel engine experimental conditions by means of reaction flow and rate-of-production analyses to 18 species and 191 reactions. To validate the mechanism, comparisons with results from the literature, from measurements at the single-cylinder diesel engine, and from shock tube measurement were made, and a good agreement was obtained. Moreover, the major formation pathways for NO₂ could be identified (M. Rößler et al., Motortechn. Z., 7, pp. 72 – 78 (2017)).

12. AN EXPERIMENTAL KINETIC STUDY FOR THE REACTION BETWEEN VINYL RADICALS ASSOCIATED PROPENE MOLECULE AND MOLECULAR OXYGEN.

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Abstract

An experimental chemical kinetic analysis concerning the bimolecular reaction between vinyl type free radicals associated with propene ($2\text{-CH}_3\text{CCH}_2^\bullet$, *cis*- $\text{CH}_3\text{CHCH}^\bullet$, *trans*- $\text{CH}_3\text{CHCH}^\bullet$) and molecular oxygen (O_2) has been carried out using tubular laminar flow reactor coupled with the photo-ionization quadrupole mass spectrometer (PIMS). Pulsed laser photolysis with the photons having the wavelength of 193nm or 248nm was used to produce a homogeneous stream of free radicals using relevant precursors. Maintaining pseudo-first order condition, a real-time radical decay signal was measured to deduce the bimolecular rate coefficients for the reactions: $2\text{-CH}_3\text{CCH}_2^\bullet + \text{O}_2$ **(1)**; *cis*- $\text{CH}_3\text{CHCH}^\bullet + \text{O}_2$ **(2)**; *trans*- $\text{CH}_3\text{CHCH}^\bullet + \text{O}_2$ **(3)**. Bimolecular rate coefficient for reactions **(1)-(3)** has a negative temperature dependence under the temperature range of 220K – 420K and becomes temperature independent as we approach the upper limit of this temperature range. Under the pressure range of 0.3torr-1.5torr rate coefficients for reactions **(1)-(3)** were independent of bath gas (He) concentration. Dominant products for reaction **(1)** were $\text{CH}_3\text{CO}^\bullet$, H_2CO and for reaction **(2)-(3)** we observed the formation of CH_3CHO , HCO^\bullet as products. Within, measured temperature range all the three reactions have their reaction mechanism analogous to the oxidation of vinyl radical ($\text{C}_2\text{H}_3^\bullet$).¹ Further comparison is carried out to understand the effect of methyl group substitution on the kinetics of $\text{C}_2\text{H}_3^\bullet$ radical oxidation. Rate coefficients observed for reaction **(1)-(3)** are also compared with the results observed by Slagle et al² (*cis-trans*- $\text{CH}_3\text{CHCH}^\bullet + \text{O}_2$) and Chen et al³ (*trans*- $\text{CH}_3\text{CHCH}^\bullet + \text{O}_2$).

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13. COMPUTATIONAL INVESTIGATIONS ON THE THERMOCHEMISTRY AND KINETICS FOR THE AUTOIGNITION OF 2-PENTANONE

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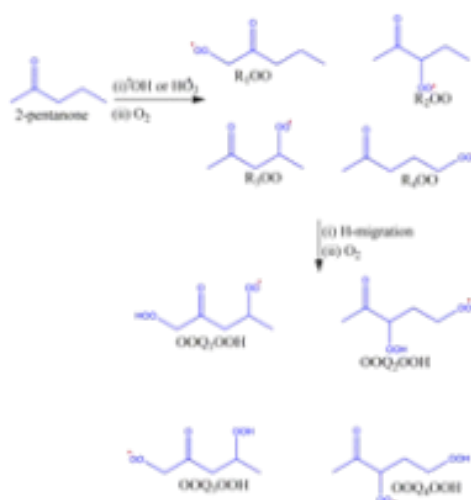
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Abstract

Ketones have been identified as products from lignocellulosic biomass conversion, which motivates to consider these compounds as biofuel candidates (H Minwegen et al., Proc. Combust. Inst, 36, 561-568, 2017). To explore the possibility of using 2-pentanone as biofuel, we have investigated the thermochemistry and kinetics for the key elementary reactions involved in autoignition and low temperature combustion by computational methods. CBS-QB3 method has been used to study the thermochemistry and energetics of all the species involved. The present study involves the unimolecular reactions of alkylperoxy (ROO^\bullet), hydroperoxyalkyl ($^\bullet\text{QOOH}$) and hydroperoxyalkylperoxy ($^\bullet\text{OOQOOH}$) radicals of 2-pentanone, as these radicals are responsible for chain branching at low temperature oxidation which can be useful in modeling the autoignition (A Miyoshi, JPCA, 115, 3301-3325, 2011). 1,6 and 1,5 H-migration reactions are the most favorable reaction pathways for ROO radicals to form their respective QOOH radicals. For $^\bullet\text{OOQOOH}$ radicals, the peroxy radical interconversion ($^\bullet\text{OOQOOH}$ to HOOQOO^\bullet) has lower energy barrier, but the decomposition proceeds with either HO^\bullet_2 -elimination or other H-migration reactions. The temperature dependent rate coefficients are studied using the canonical variational transition state theory (CVT) with small curvature tunneling (SCT) in the wide temperature range of 400 – 2500 K.



14. DEVELOPMENT OF A METHODOLOGY FOR THE CHEMICAL CHARACTERIZATION OF SOLUBLE ORGANIC FRACTION (SOF) OF THE PARTICLES GENERATED FROM (BIO)FUELS COMBUSTION USING GC-MS/MS

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Abstract

The incomplete combustion processes contribute to a great extent generating atmospheric pollutants, not only in gas phase but also particles in suspension. The main source of particulate matter is the traffic (A. May et al., Atmos Environ, 88, pp. 247-260 (2014)). The use of biofuels are incrementing because of the law is more restrictive (Euro VI). Their emissions are constituted for soot that is mainly composed of black carbon and a soluble organic fraction where organic compounds are adsorbed on it such as Polycyclic Aromatic Compounds (PACs). They are considered as toxic persistent substances (WHO, 2010). The soot has been classified like second contribution more strong to the climate change after CO₂ (IPCC, 2013). Therefore, to know the chemical composition of soot is important to evaluate its impact on human health and the climate change.

In this study, an analytical methodology has been developed, optimized and validated for the extraction and analysis of 28 PACs (PAH, nitro-PAH and oxy-PAH) from soot particles using Printex-U (considered as a good representative of diesel soot) and a standard reference material (SRM) NIST 1650b. Four blends of solvents were tested in order to simultaneously extract all PACs using microwave assistant extraction (MAE). PACs were quantified with GC-MS/MS operating in Multiple Reaction Monitoring (MRM) mode. Two transition per PAC were selected, one for quantification and another for qualification. The validation was carried out using three blends of solvents: pyridine:acetic.acid, acetone:toluene and dichloromethane. The results showed that the best solvents was acetone:toluene getting a precision from 1 to 20%. The recoveries were from 66 to 152% except for benzo(b)fluoranthene and Chrysene that were 183 and 171% respectively. This method was applied to a diesel soot sample. The results showed that SRM 1650b and diesel soot present differences regarding the adsorption of the heaviest and nitro-PAH since the recoveries of internal standards were 48-218% for SRM while for diesel soot were 1-41%. Soxhlet extraction was also carried out improving the recoveries (15-51%) of the diesel soot.

15. A COMPARATIVE HIGH-PRESSURE SHOCK TUBE STUDY ON THE IGNITION OF PENTANOL ISOMERS: 1-, 2- AND 3- PENTANOL

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Abstract

The concern over air pollution from combustion and fossil fuel shortage increased the research around biofuels as an alternative source of energy. 1-, 2- and 3-pentanol have many advantages over ethanol, their high energy densities, lower vapor pressures, low miscibility in water and good solubility in gasoline or Diesel fuel. Despite good qualities as biofuels, linear pentanol combustion have not yet been comprehensively studied in shock tube¹⁻⁴. In the present study, the authors investigated ignition behavior behind a reflected shock wave for three linear pentanol isomers (1-pentanol, 2- pentanol and 3-pentanol) at high pressure. The goal of the present work is to understand the impact of the alcohol group position on the ignition of the pentanols. Experiments were conducted over a large range of temperatures (1000 to 1480 K), pressures (20 and 40 bar) and equivalence ratios (0.5, 1 and 2). The O₂ concentration in the mixtures fuel/O₂/Ar varies from 3.75 % to 15 % to preserve the fuel concentration at 1 %. Ignition delay times follow a standard Arrhenius law over the investigated conditions. Ignition delay times increase with equivalent ratios and decrease with the increase of temperature and pressure. The three isomers can be ranked according to their ignition delay, the less reactive being 2-pentanol and the most reactive 1-pentanol for all the experimental conditions. The global activation energy of all three isomers is the same as the experimental data have the same slope.

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16. JET-STIRRED LOW-TEMPERATURE OXIDATION OF n-PENTANE: THE EFFECT OF NO_x ADDITION

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Abstract

An effective technique, already implemented in new combustion techniques such as low-temperature combustion and homogeneous charge compression ignition to reduce the production of pollutants such as NO_x and soot, consists of recycling the exhaust gas back into the engine system, so-called exhaust gas recirculation. In this way, reactants are diluted with exhaust gases (CO₂, H₂O, NO_x, SO₂...), working under high dilution and low temperature conditions. Previous studies have analyzed the interaction between NO and different fuels, indicating that NO can promote or inhibit fuel consumption depending on the operating conditions. N-pentane is one of the smallest alkanes which presents a low-temperature reactivity and it is an intermediate during the oxidation of higher hydrocarbons.

In this context, the impact of the NO and NO₂ addition has been investigated during the n-pentane (10000 ppm) low-temperature (500-900 K) oxidation in a jet-stirred reactor under stoichiometric conditions. Different NO and NO₂ mole fractions in the reactant mixture have been investigated: 0, 500 and 1000 ppm for NO; 0 and 400 ppm for NO₂. The residence time was kept constant at a value of 2 s and argon has been used as carrier gas.

The results indicate that the onset temperature for n-pentane consumption is shifted by the addition of NO from 575 K (without NO_x) to 650 K (500 ppm NO) or 690 K (1000 ppm NO), and the characteristic NTC region is completely suppressed for 1000 ppm of NO. The addition of NO₂ does not alter the n-pentane low-temperature oxidation. However, n-pentane high-temperature oxidation is accelerated by the presence of NO or NO₂.

The coupling of the jet-stirred reactor with a continuous wave Cavity Ring Down Spectroscopy has allowed the detection and quantification of HONO for the first time under a combustion environment. The behavior of this notable intermediate nitrogen species is not fully understood, thus the detection and quantification of HONO is considered of great value.

A detailed chemical kinetic mechanism has been compiled to describe the experimental trends observed, but kinetic efforts still have to be made to fully understand the impact of NO_x addition on the low-temperature oxidation of n-pentane.

Acknowledgements

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17. EVALUATION OF DME AS A POSSIBLE FUEL ADDITIVE THROUGH THE STUDY OF THE HIGH-PRESSURE OXIDATION OF ITS MIXTURES WITH ACETYLENE

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Abstract

Nowadays there is an increasing motivation to search new energy sources more environmental friendly, such as alternative fuels which result in less pollutant emissions. Dimethyl ether (DME) has attracted a lot of interest as an alternative fuel, especially for engines, due to its high cetane number, rich oxygen content, the absence of C-C bonds in its molecular structure, almost immediate vaporization, and lower ignition temperature compared to diesel fuel. On the other hand, acetylene (C_2H_2) has been widely considered as an important soot precursor due to its role in the HACA route which explains soot formation from PAHs.

In this context, the present work includes an experimental and modeling study of the high-pressure (20, 40 and 60 bar) oxidation of C_2H_2 and DME mixtures. This study will allow a greater knowledge of the influence that DME addition may have on the behavior of a soot precursor during its oxidation. The experimental study of the oxidation of C_2H_2 (1000 ppm) and DME (100 or 400 ppm) mixtures has been carried out in a flow reactor, in the 450-1050 K range and for different air excess ratios (λ). The chemical kinetic mechanism used in this work has been compiled during the last years by our research group with the GADM mechanism (P. Glarborg et al., *Combust. Flame*, 115, pp. 1-27 (1998)) as basis, and progressively updated and modified to consider the high-pressure conditions and the different compounds involved. The last version of this mechanism successfully describes the DME oxidation (L. Marrodán et al., *The inhibiting effect of NO addition on dimethyl ether high-pressure oxidation*, Submitted, (2018)). There is a good agreement between experimental results and modeling calculations. Results indicate that increasing the pressure shifts to lower temperatures the onset temperature for both C_2H_2 and DME consumption. The addition of different amounts of DME to a given concentration of C_2H_2 has no significant implications, except for the highest value of λ and DME concentration analyzed, for which the conversion of C_2H_2 starts at lower temperatures.

Acknowledgements

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18. EXPERIMENTAL INVESTIGATION OF BUTANOIC AND PENTANOIC ACID OXIDATION

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Abstract

Biomass conversion into bio-oil is one of the viable answer to energy issues. The use of this renewable fuel can be an alternative to fossil fuels; however their unstable composition is one of the barriers for a complete understanding of their behavior and especially in combustion. Carboxylic acids are a non-negligible part of bio-oils but their decomposition under oxidation and pyrolysis conditions are still not well understood. The high number of experimental issues (viscosity, high boiling point, dimerization in gaseous phase...) can explain the lack of experimental data concerning acids heavier than acetic acid. But the role of the carboxylic acids as intermediate in the decomposition of other products present in bio-oil (alcohols, aldehydes) has increased the need of experimental data in order to validate a kinetic model for these compounds.

That is why an experimental study of butanoic acid combustion and pentanoic acid pyrolysis and combustion were performed. These experiments have been carried out in a jet-stirred reactor over the temperature range 700–1100 K, at a residence time of 2 s, pressure of 106.7 kPa, inlet fuel mole fraction of 0.002 for the pyrolysis and 0.005 for the combustion at three equivalence ratios ($\phi=0.5, 1$ and 2). Gas chromatography analysis coupled with various detectors (Flame Ionization Detector, Thermal Conductivity Detector and Mass Spectrometer) was used to identify and quantify the oxidation products and the fuel conversion. Around 40 species were observed during the oxidation and pyrolysis of pentanoic acid and around the half for butanoic acid oxidation. One of the main results of this study is the observation of an early production of CO₂ compared to that of CO under each conditions studied for each fuels.

The final aim of this study is to propose a kinetic model for butanoic and pentanoic acid combustion and pyrolysis and to implement it in a larger model considering some other species present in bio-oils.

Acknowledgements

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19. KINETIC CHARACTERISTICS RELATED TO PARTICULATE MATTER FORMATION IN BIOMASS COMBUSTION

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Abstract

Over a decade biomass is considered as the largest and sustainable energy resource due to its huge availability and applicability, and low net CO₂ emissions (Jones et al. 2014). According to the recent European regulation, emissions of small-scale combustion devices must comply with the admissible limits (Directive 2016/2284/EU). Despite the effort done in optimizing the combustion process of the small scale devices, operating with solid biofuels there is still great concern about the ambient air quality in the settlements, where central heating or alternative energy sources are not available or are inaccessible due to different socio-economic factors. Significant number of the European population is exposed to exceeded levels of different pollutants that are mainly products of the incomplete combustion. Thus the European commission (EC) has undertaken series of activities aiming to protect the citizens from the uncontrolled air pollution see e.g. (EC - Press release).

The major objective of the current study is the characterization of the chosen biomass fuels, currently being produced and offered at the Bulgarian biomass market, through determination of their key chemical-kinetic and physical properties. Thus the biomass solid fuels were first characterized through detailed chemical analyses then the main gas phase products were measured together with the time history and the size distribution of the PMs in the flue gas during single pellet combustion in a Formation Rate Unit (FRU) reactor described in (Winter F. et al. 1990, Löffler G et al. 2001).

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20. THE COMPLEXITY OF IGNITION PHENOMENA IN DIETHYL ETHER/AIR MIXTURES

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Abstract

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

In our contribution, we present a DEE oxidation mechanism that is valid over a broad range of temperatures from 500 to 1300 K (J. Eble et al., *Z. Phys. Chem.* 231 (2017) 1603). It consists of a base mechanism taken from Metcalfe et al., *Int. J. Chem. Kinet.* 45 (2013) 638, and a DEE-specific extension. The mechanism was validated over wide ranges of temperature and pressure by modeling experimental data from the literature with special attention paid to the above-mentioned different ignition characteristics.

With the validated mechanism, DEE autoignition in a spherical vessel was simulated for different temperatures and pressures by using the program code INSFLA (see e. g. U. Maas and J. Warnatz, *Combust. Flame* 74 (1988) 53). Species concentrations and temperature were calculated as a function of time and position for the one-dimensional laminar problem with isothermal walls, where mass and energy transport have been taken into account.

In this way, a simulation and characterization of different ignition phenomena like one-stage ignition, multiple-stage ignition and cool flames was possible. It turned out, however, that a distinct and unique classification of ignition phenomena was difficult. As a consequence, we propose three possible criteria for the analysis of ignition phenomena, namely the temperature-, pressure- and concentration-criteria. We give examples for the different ignition phenomena, discuss their appearance, and map the corresponding p,T -ignition diagrams.

21. LASER PHOTOLYSIS KINETIC STUDIES OF METHYL TERT-BUTYL ETHER WITH OH AT LOW TEMPERATURES RELEVANT TO COMBUSTION

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Abstract

Methyl tert-butyl ether (MTBE) has been used as a replacement for lead-based anti-knock additives, and as an octane rating enhancer in gasoline, due to its oxygenated structure. MTBE improves the cleanliness and efficiency of gasoline combustion by reducing the formation of CO and soot particulates. Due to current ambitious targets set for CO₂ emissions reduction, biofuels are a potential alternative to conventional fuels. Ethers show promise as a potential biofuel, with MTBE being one of the suitable candidates due to its high energy density and compatibility with current engine technology.

In addition, novel engines, such as homogeneous charge compression ignition (HCCI) engines, rely on an understanding of the low temperature combustion mechanisms of the fuel in order to run efficiently. We have therefore studied various aspects of MTBE chemistry via reactions with OH, in the absence and presence of O₂.

Laser flash photolysis – laser-induced fluorescence has been used to study the kinetics of the reaction between MTBE and the hydroxyl radical, OH. The bimolecular rate coefficient for this reaction has been determined over 298 – 727 K at 29 – 67 Torr. The temperature dependence of the rate coefficient can be parameterised as:

$$k(298 - 680 \text{ K}) = (0.58 \pm 1.63) \times 10^{-11} \left(\frac{T}{298} \right)^{1.45 \pm 1.93} \exp \left[\frac{-1837 \pm 7190}{RT} \right]$$

Our measurements are in good agreement with previous work in the poorly characterised low temperature region that is crucial to understanding biofuel combustion in HCCI engines. Regeneration of OH was observed in the presence of oxygen, above approximately 568 K, and was manifested in the form of biexponential decays. At low [O₂], the yields of OH were significantly lower than for DME; these results can be rationalised by the barriers for decomposition of the different R-O-CH₂ radicals. At higher [O₂], the yield of OH increases as more R-O-CH₂ radicals are converted to RO₂ and QOOH.

22. A COMPARATIVE HIGH-PRESSURE JET-STIRRED REACTOR STUDY ON THE OXIDATION OF PENTANOL ISOMERS: 1-, 2- AND 3-PENTANOL

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Abstract

Compared to ethanol, higher alcohols have received attention as they can be considered as alternative biofuels thanks to their higher energy content and as they present less mixing issues with conventional fuels. In this context, primary alcohols such as 1-pentanol, iso-pentanol and 2-methyl-1-butanol were studied in the literature, the related jet-stirred reactor studies can be found in [1–3]. In this study, the oxidation of two secondary alcohols, namely pentan-2-ol (2-pentanol) and pentan-3-ol (3-pentanol) were investigated under the same conditions of 1-pentanol [1]. The experiments were carried out at 10 atm, between 730–1180 K and for equivalence ratios between $\varphi = 0.35$ –4. The aim is to see the effect of the position of the –OH group on the global reactivity and on product distribution. A chemical kinetic mechanism is also used and tested against the present data. For this purpose sub-mechanisms of 2- and 3-pentanol were developed and integrated into an existing mechanism including alcohols. Given their structure, 2- and 3-pentanol produced C₅ ketones as important intermediates as opposed to pentanal in the case of 1-pentanol. Also these secondary amyl alcohols were found to show less reactivity compared to 1-pentanol in terms of fuel decomposition.

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23. KINETIC STUDIES OF TERT-BUTANOL UNDER LOW TEMPERATURE COMBUSTION CONDITIONS

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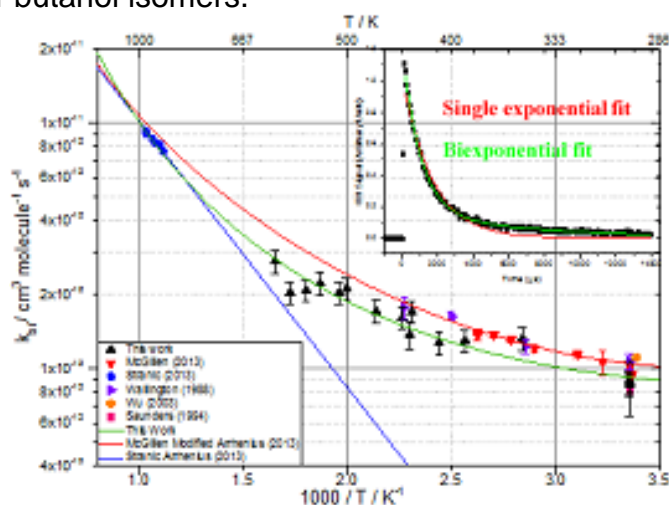
Abstract

The isomers of butanol have recently received interest as potential alternative biofuels, and can be made via a range of fermentation methods. The bio-butanols demonstrate several key advantages over other biofuels, such as being more energy dense and less corrosive than competitors such as bioethanol.

There currently exists a large gap in the kinetic data at relevant low temperature combustion conditions for the reactions of the different isomers of butanol with OH, a key reaction in the combustion of the potential fuels in an engine. Using the pulsed laser photolysis – laser induced fluorescence (PLP-LIF) method, the bimolecular rate coefficients for the reaction of OH with the butanol isomer tert-butanol have been measured over the temperature range 298 – 605 K at 30 – 90 Torr. The temperature dependence of the rate coefficient can be defined as:

$$k(T) = ((2.86 \pm 4.77) \times 10^{-23}) \times T^{3.72 \pm 0.21} \times \exp\left(\frac{-7441 \pm 1008}{R \times T}\right)$$

At higher temperatures, abstraction at the β site in butanols leads to OH regeneration from decomposition of the radical to OH + alkene and biexponential OH decays are observed. Analysis of these decays allows for a determination of site specific abstraction rate coefficients. Here, tert-butanol has been used as an example of a simple alcohol due to its branched structure, providing a good basis for further studies of the other butanol isomers.



24. ACETYLENE ADDITION TO VINYL AND ARYL RADICALS: EXPERIMENTAL INVESTIGATION OF HACA AND PAH FORMATION PATHWAYS

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Abstract

Kinetic models of combustion and pyrolysis processes are often highly sensitive to bimolecular rate coefficients and product branching ratios for radical-molecule reactions. Experimental measurements of such reactions are scarce due to the transience of reaction intermediates, particularly under combustion-relevant conditions. While transient absorption spectroscopy is a reliable method to determine the rates of radical reactions, no information is obtained about product branching or secondary chemistry.

The Chemical Dynamics Laboratory at MIT has developed a unique apparatus for the simultaneous detection of

- 1) photolytic generation and decay of the radical reactant by laser absorption spectroscopy and
- 2) mass- and time-resolved products by VUV-PIMS.

This apparatus was used to investigate the addition of acetylene molecules to vinyl radical. The VUV-PIMS product measurements show evidence of temperature and pressure dependent branching to the hydrogen loss and adduct stabilization channels, as well as formation of benzene following a second acetylene addition to the 1,3-butadiene-1-yl radical adduct. These results indicate that stable products of secondary reactions can be detected and quantified using our apparatus. The hydrogen-abstraction-acetylene-addition (HACA) mechanism, of key importance in the formation of polycyclic aromatic hydrocarbons (PAH), can lead to ring closing via sequential acetylene additions; quantitative measurements of the HACA and ring-closing steps for aromatic radicals are thus invaluable for validating combustion models. VUV-PIMS results for bimolecular reactions of acetylene and aromatic radicals (phenyl, naphthyl) and comparison with the predicted product branching from ab initio calculations will be discussed.

25. THE SENSITIZING EFFECTS OF NO₂ AND NO ON METHANE LOW TEMPERATURE OXIDATION IN A JET STIRRED REACTOR

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Abstract

The mutual effects of CH₄/NO_x have attracted considerable attention in the past decade. Despite the abundant experimental reports concerning the hydrocarbon-NO_x interactions, the sensitizing effects of NO₂ on methane low-temperature oxidation in a jet-stirred reactor has not been performed yet. Additionally, the knowledge of some notable intermediate nitrogen species (such as HONO) is not comprehensively understood. In this context, the oxidation of neat methane and methane doped with NO₂ or NO in argon at 107 kPa and temperatures between 650-1200 K with a fixed residence time of 1.5 s has been investigated in a jet-stirred reactor for different equivalence ratios (Φ), ranging from fuel-lean to fuel-rich conditions. Four different diagnostics were used: gas chromatography (GC), chemiluminescence NO_x analyzer, continuous wave cavity ring-down spectroscopy (cw-CRDS) and Fourier transform infrared spectroscopy (FTIR). In case of the oxidation of neat methane, the initial oxidation temperature was above 1025 K while it shifted to 825 K with the addition of NO₂ or NO, independently of equivalence ratio. This indicates that the added NO₂ or NO highly promotes methane oxidation. The consumption rate of methane exhibits a similar trend with the presence of both NO₂ and NO. The search for HONO and CH₃NO₂ species has been attempted. A detailed kinetic mechanism, derived from POLIMI kinetic framework, is used to interpret the experimental data. The agreement between the experimental data and model predictions is very satisfactory. Reaction rate and sensitivity analysis were conducted to illustrate the kinetic regimes. The fact that the additions of NO and NO₂ seem to have similar effects on promoting methane oxidation can be explained by the fact that both species are involved in a reaction cycle interchanging them and whose result is $2\text{CH}_3 + \text{O}_2 = 2\text{CH}_2\text{O} + 2\text{H}$. Additionally, the direct participation of NO₂ in the $\text{NO}_2 + \text{CH}_2\text{O} = \text{HONO} + \text{HCO}$ reaction has a notable accelerating effect on methane oxidation.

The work leading to this intervention has received funding from the European Union Horizon H2020 Programme (H2020-SPIRE-04-2016) under grant agreement n°723706

26. EXPERIMENTAL AND MODELLING STUDY OF THE MULTICHANNEL THERMAL DISSOCIATIONS OF CH₃F AND CH₂F

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Abstract

The thermal unimolecular dissociation of CH₃F was studied in shock waves by monitoring the UV absorption of a dissociation product identified as CH₂F. It is concluded that the formation of this species corresponds to a minor, spin-allowed, dissociation channel of about 3 % yield. Under the studied conditions near to the low-pressure limit of the reaction, on the other hand, the energetically most favourable dissociation leads to ³CH₂ + HF on a dominant, spin-forbidden, pathway. By considering the multichannel character of the reaction, it is shown that, in contrast to the low-pressure range, the high-pressure range of the reaction should be dominated by CH₂F formation. The channel-switching probably takes place at pressures somewhat higher than those applied in the present work.

In addition to the two dissociation channels of CH₃F producing ³CH₂ + HF and CH₂F + H, a third, spin-allowed, dissociation channel leading to ¹CHF + H₂ was also considered and shown to proceed with a yield smaller than 0.5 %. Besides the dissociation of CH₃F, the dissociation of CH₂F was studied by monitoring the UV spectrum of CH₂F. Details of this spectrum as well as the spectrum of the dissociation product CF were investigated. Similar to CH₃F, the dissociation of CH₂F can proceed on several dissociation channels, under the present conditions predominantly to CF + H₂. After modelling single-channel falloff curves for all reaction pathways, coupling effects were interpreted in the framework of multichannel unimolecular rate theory.

28. HIGH-PRESSURE LOW-TEMPERATURE OXIDATION OF DIETHYL ETHER COMPARED TO N-PENTANE AND THEIR MIXTURE

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Abstract

The present work provides for the first time detailed species profiles obtained at high pressure for the low-temperature (LT) oxidation of diethyl ether (DEE), a promising biofuel. High-pressure effects on the DEE oxidation behavior were examined. DEE was then compared to its corresponding linear five-heavy-atom hydrocarbon fuel, i.e. n-pentane, to point out the influence of the fuel structure on their LT oxidation behavior. Finally, the oxidation of a mixture composed of these two fuels was investigated at different pressures to investigate simultaneously the interaction of fuels and the effects of the pressure.

Experiments were performed for stoichiometric mixtures, residence time of 2 s, pressure range of 2-10 bar and temperatures of 400-1100 K, using a setup of a high-pressure jet-stirred reactor coupled to gas chromatography. About 20-30 species at each condition were detected. Furthermore, a photoionization molecular-beam mass spectrometer was also used to track the effect of fuel additives on the composition of fuel-specific isomers. Based on our previous development, a combined LT kinetic model was updated with considering cross reactions between these two fuels. It was tested with these high-pressure data, showing a good predictive capacity, and subsequently assisting in the data interpretation.

Both experimental and modelling results show that: (i) Compared to 1 bar, high pressure does not significantly affect the starting reaction point of DEE, but it strongly increases the global reactivity of this fuel and alters species formation. High pressure reduces negative temperature coefficient zones. (ii) Compared to n-pentane, DEE starts to react at much lower temperatures and it has a much weaker NTC as well as a significant difference in LT product distribution. Some analogous reaction classes, that are very important for the LT DEE oxidation, do not seem to be applicable for the case of n-pentane. (iii) DEE addition enhances strongly the reactivity of n-pentane in the fuel mixture. (iv) The reactor pressure significantly influences the reactivity of the fuel mixture in the range of 2.5-7 bar, however this influence becomes very weak when the pressure increases from 7 to 10 bar.

Luc-Sy Tran is grateful to the COST Action CM1404 (ref. STSM-CM1404-100117-082308) and the Alexander von Humboldt-Foundation for financial support.

29. THE OXIDATION OF FURFURAL IN A JET-STIRRED REACTOR: A COMBINED EXPERIMENTAL AND MODELING APPROACH

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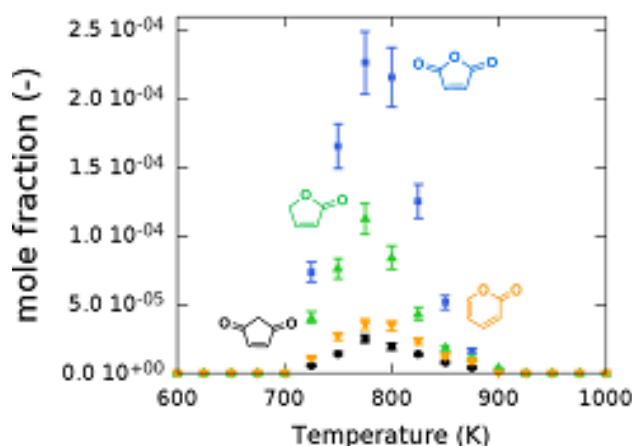
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Abstract

The fast pyrolysis of biomass is a trendy topic in recent studies regarding the need for fuels and chemicals from renewable resources. Furfural is identified as one of the major compounds produced during the pyrolysis of biomass. Only one experimental study on furfural oxidation is reported by Thornton et al. in a jet-stirred reactor at temperatures of 1000-1300K. This dataset is limited to higher temperatures and does not include the initial oxidation products of furfural. For this reason, the oxidation of furfural is studied in a jet-stirred reactor at atmospheric pressure and temperatures of 600-1000K. Stoichiometric ($\phi=1.0$) and fuel-lean ($\phi=0.5$) conditions are considered for an average residence time of 2s and a furfural inlet mole fraction of 0.005.

The conversion of furfural starts at 725K and 675K for $\phi=1.0$ and 0.5 respectively. As expected from the molecular structure of furfural, no low-temperature oxidation is observed. Theoretical calculations have confirmed that, after the addition of molecular oxygen to the furfural radicals, the barrier for isomerization is similar to or higher than the re-dissociation channel. The main intermediate species detected are lactones. The mole fraction profiles of these species as a function of temperature are given in the figure. Automatic kinetic model generation together with theoretical calculations will be used to find the most important pathways for the formation of these intermediates and other final oxidation products.



30. KINETICS OF OH RADICAL REACTIONS WITH 2,5-DIMETHYLFURAN

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Abstract

Furans are a class of cyclic ethers with potential for use as biofuels¹, particularly 2,5-dimethylfuran (DMF) which has a similar energy density to gasoline.² Produced from waste biomass, furans do not come into competition with food crops and therefore do not threaten global food security. Knowledge of the kinetics and mechanisms of the oxidation chemistry of furans will improve the predictive capabilities of combustion mechanisms to aid investigations of their potential use as fuels and the possible impacts of increased use on atmospheric chemistry and composition.

This work reports the kinetics of the reaction between the OH radical and 2,5-dimethylfuran over a range of temperatures (298-680 K) and pressures (10-150 Torr). Experiments using flash photolysis of H₂O₂/N₂/DMF gas mixtures were performed under pseudo-first-order conditions, with monitoring of OH radicals by laser-induced fluorescence (LIF) spectroscopy.

The OH + DMF reaction exhibits pressure-dependent kinetics with a negative temperature dependence observed over the temperature and pressure ranges investigated. Fits to the data indicate a low pressure limit of $k_0 = (9.41 \pm 6.40) \times 10^{-29} \exp((1596 \pm 263)/T) \text{ cm}^6 \text{ s}^{-1}$ and a high pressure limit of $k_\infty = (1.11 \pm 0.06) \times 10^{-11} \exp((718 \pm 19)/T) \text{ cm}^3 \text{ s}^{-1}$.

The potential energy surface of the reaction has also been investigated at the M06-2X/cc-pVTZ level of theory, and indicates that addition of OH to DMF is dominant under the experimental conditions of this study. Optimisation of the potential energy surface for the dominant addition channel using the Master Equation Solver for Multi-Energy well Reactions (MESMER)³ shows the addition product lies 156.4 kJ mol⁻¹ - below the entrance channel. The calculations show that the abstraction channels increase in importance at temperatures above 900 K. Implications of the results will be discussed.

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32. RATE CONSTANTS OF THE REACTIONS OF $\text{DO}_2 + \text{DO}_2$ AND $\text{HO}_2 + \text{DO}_2$

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Abstract

The hydroperoxy radical HO_2 is a key species in many chemical processes both in the gas phase and in the heterogeneous phase. It plays a central role in atmospheric chemistry. Its responsibility in cycles of destruction of stratospheric ozone as well as its ability to oxidize the main VOCs of the troposphere through its coupling with OH can be mentioned. Understanding the mechanisms involving HO_2 requires the development of tools capable of detecting and quantifying this radical in its environment. The DO_2 radical does not play any role in atmospheric chemistry, but a selective detection is nevertheless highly desired in laboratory studies for carrying out mechanistic studies, especially involving hydrogen abstraction mechanisms.

The reactions of $\text{DO}_2 + \text{DO}_2$ and $\text{DO}_2 + \text{HO}_2$ have been studied by the simultaneous, selective and quantitative measurement of HO_2 and DO_2 by cw-CRDS in the near infrared (Assaf et al., 2017), coupled to a radical generation by laser photolysis. DO_2 was generated by photolysing Cl_2 in the presence of CD_3OD . Low concentrations of HO_2 (less than 10% of the total radical concentration) were also generated, probably due to the presence of small amounts of CD_3OH , obtained through fast isotope exchange between CD_3OD and residual H_2O , always present on tubing and reactor walls. The rate constant of the DO_2 self reaction was found to be $6.7 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$, in good agreement with literature data (Martin and Thrush, 1988). This work presents the first determination of the rate constant for the cross reaction, $\text{HO}_2 + \text{DO}_2$. A pressure dependent rate constant was found with $k = (2.1 \pm 0.5) \times 10^{-12} + (5.5 \pm 2.0) \times 10^{-31} [\text{He}] \text{ cm}^3 \text{ s}^{-1}$, presenting a 50 and 12 times stronger pressure dependence than the self reactions of DO_2 and HO_2 , respectively. Use of the symmetry rule exhibits an excellent agreement for the bimolecular rate constant of $\text{HO}_2 + \text{DO}_2$, when using the literature values for $\text{DO}_2 + \text{DO}_2$ and $\text{HO}_2 + \text{HO}_2$ (Assaf et al., to be submitted).

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33. ATMOSPHERIC CHEMISTRY OF $n\text{-CH}_3(\text{CH}_2)_x\text{CN}$ ($x = 0\text{-}4$) AND $n\text{-CH}_2=\text{CH}(\text{CH}_2)_x\text{CN}$ ($x = 0\text{-}4$): KINETICS AND MECHANISMS

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Abstract

Smog chamber/Fourier transform infrared (FTIR) techniques were used to investigate the atmospheric chemistry of $n\text{-CH}_3(\text{CH}_2)_x\text{CN}$ ($x=0\text{-}4$) [1,2] and $n\text{-CH}_2=\text{CH}(\text{CH}_2)_x\text{CN}$ ($x=0\text{-}4$) [3]. The kinetics of the nitriles was investigated with respect to reaction with Cl atoms, OH radicals and O₃. Trends in the kinetic results of $n\text{-CH}_3(\text{CH}_2)_x\text{CN}$ ($x=0\text{-}4$) have shown to be similar to kinetic data for other substituted alkanes. Reaction mechanisms have been investigated using Cl atoms to initiate the oxidation. Multiple products such as NCC(O)OONO₂, ClC(O)OONO₂, HC(O)CN, HC(O)Cl, HCN, CH₃C(O)CN, and CH₂ClC(O)CN could be determined from the shorter nitriles; CH₃CN, CH₃CH₂CN, and CH₂=CHCN. The oxidation of the longer nitriles gives multiple different oxygenated products, which have not been possible to distinguish from each other. From the OH radical rate constants atmospheric lifetimes have been estimated for all the compounds.

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34. ATMOSPHERIC OXIDATION OF CH₃OOH AND CH₃OOOH BY OH

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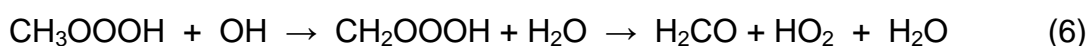
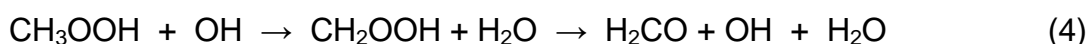
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Abstract

Methyl peroxy radical (CH₃O₂) is a key specie in the Earth's atmosphere, and one of its main sinks involves reaction with HO₂, producing CH₃OOH (reaction 1).¹ Very recently it has been shown that methyl peroxy radical reacts with hydroxyl radical (reaction 2), and that this reaction can compete with the oxidation by hydroperoxyl radical.²⁻³ Therefore both reactions play an important role in the Earth's atmosphere.



The atmospheric lifetime of CH₃OO is estimated to be 1-4 days, and one of its main sinks is oxidation by hydroxyl radical.⁴ CH₃OOOH is estimated to be stabilized up to 35%⁵ and therefore its oxidation may play an important role in the chemistry of the Earth's atmosphere. It is well known that the reaction of CH₃OO with OH follows reactions 3 and 4, and we have performed a theoretical investigation on the reaction mechanism, considering the effect of the relative humidity on these processes.⁶ The reaction of CH₃OOOH with OH is unknown, and we have found that it follows reactions 5 and 6.



For reactions 3 and 4 our computed rate constants are 3.59×10^{-12} and 1.68×10^{-12} cm³·molecule⁻¹·s⁻¹, respectively at 298 K, in very good agreement with the experimental values. Our calculations also show that at very hot and humid conditions reaction 3 and 4 are enhanced up to 19% and 5.6%.⁶ The reaction between CH₃OOOH with OH is faster and our computed rate constants for reactions 5 and 6 are 2.05×10^{-11} and 1.54×10^{-12} cm³·molecule⁻¹·s⁻¹, respectively at 298 K.

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35. KINETIC STUDY OF SATURATED ALCOHOLS DURING DAY-TIME: REACTIVITY OF 3,3-DIMETHYL-1-BUTANOL AND 3,3-DIMETHYL-2-BUTANOL

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Abstract

Alcohols are present in the atmosphere from a wide variety of antropogenic and biogenic sources (Calvert, J. et al. Oxford University Press, (2011)). The interest of saturated alcohols have been increasing during the last decades due to their use as alternative energy sources in automotive sector (Rajesh and Saravanan, *Renew SustEnerg Rev*, pp 84-115, (2016)). According to literature, the main degradation route of saturated alcohols in the atmosphere is the reaction with OH radicals during day time (Atkinson and Arey, *Chem. Rev.*, pp 4605–4638 (2003)). Gas-phase reactivity of 1-butanol, 2-butanol and its derivatives have been previously studied (IUPAC <http://www.iupac-kinetic.ch.cam.ac.uk/>). However there is a lack of information regarding the diurnal reactivity of 3,3-dimethyl-1-butanol (3,3DM-1-BuOH) and 3,3-dimethyl-2-butanol (3,3DM-2-BuOH).

In this work, rate coefficients for the reaction of 3,3-dimethyl-1-butanol and 3,3-dimethyl-2-butanol with Cl and OH have been obtained at room temperature (~ 298 K) and 700±1 Torr. A relative technique has been employed, comparing the rates of decay of the reactant relative to that of a selected reference compound. A Fourier Transform Infrared Spectroscopy has been used as detection system.

An example of a graphical representation of equation (1) for the reaction of 3,3DM-1-BuOH and 3,3DM-2-BuOH with the two reference compounds employed is shown in figure 1 where $[S]_0$ and $[R]_0$ are the initial concentrations of substrate and reference compound, respectively, and $[S]_t$ and $[R]_t$ the concentrations of substrate and reference compound at time t , respectively. The results obtained in this work show that the main sink of 3,3DM-1-BuOH and 3,3DM-2-BuOH in the troposphere is the reaction with OH, which leads to lifetimes between 13-25 hours. For the first alcohol, reaction with chlorine atoms seems to be also important, especially in coastal areas where peaks of concentration of chlorine atoms have been observed (1×10^5 atoms cm^{-3} , Spiecer et al., *Nature*, pp 353-356 (1998)). Under these conditions the estimated tropospheric lifetime (τ_{Cl}) decreases to 10 and 23 hours for 3,3DM-1-BuOH and 3,3DM-2-BuOH, respectively.

36. STRUCTURE-REACTIVITY EVALUATION PANEL FOR GAS-PHASE ATMOSPHERIC REACTIONS OF ORGANIC COMPOUNDS

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Abstract

The objectives of this project is to bring together an expert panel to evaluate the structure-reactivity (SAR) relationships or estimation methods needed to develop detailed gas-phase chemical mechanisms or organic compounds and intermediates in the atmosphere, and make recommendations for approaches judged to be the most consistent with available knowledge. The efforts of the panel members are funded by in-kind support from their own institutions or projects, with funds provided by the Coordination Research Council to cover travel and administrative costs.

During the first year of this project, a panel was assembled representing expertise in atmospheric chemical mechanism development, SAR development; combustion mechanism development; experimental kinetic data evaluations; experimental and theoretical studies of rate constants, mechanisms, and photolysis reactions; thermochemistry; and automated mechanism generation systems. The initial members include: Bernard Aumont, Ian Barnes (now deceased), Joseph Bozzelli, William Carter, Mark Goldman, William Green, Sasha Madronich, Max McGillen, Wahid Mellouki, John Orlando, Benedicte Picquet-Varrault, Andrew Rickard, Dudley Shallcross, William Stockwell, Luc Vereecken, and Tim Wallington.

The major accomplishment during the first year of the project was the preparation of the journal article "Perspective on Mechanism Development and Structure-Activity Relationships for Gas-phase Atmospheric Chemistry", International Journal of Chemical Kinetics, in press. This will be discussed in Tim Wallington's invited presentation at this workshop, and copies will be made available with this poster. In addition, ongoing projects are being carried out in the following areas: Experimental and theoretical rate constant and product yield data collection for SAR development; Evaluation of SARs for bimolecular atmospheric reactions of organics and for atmospheric reactions of organic radicals; Estimates for photolysis reactions and treatment of photolysis in models; and Thermochemical data and estimates needed for SAR and mechanism development.

The poster will give more information about this panel and accomplishments and plans for the coming year. Those are interested in learning more and participating in this project are invited to contact the author of this poster or any of the project participants present at this workshop.

37. REACTIVITY OF NO₃ RADICAL WITH RAMIFIED UNSATURATED ALDEHYDES: THEORETICAL APPROACH FOR KINETIC AND MECHANISTIC STUDIES

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Abstract

The nitrate radical is known to be the dominant night-time oxidant of organic species in the atmosphere especially with unsaturated compounds. Among these compounds, unsaturated aldehydes are directly emitted by several anthropogenic (incomplete combustion of fuels, smokes) and natural (vegetation, forest fires) sources (*P. Carlier et al., Atmos. Environ. 20, pp. 2079-2099 (1986)*; *D. Grosjean et al., Environ. Sci. Technol. 35, pp. 45-53 (2000)*) but also produced in the atmosphere from the photo-oxidation of terpenes and conjugated dienes (*A. Calogirou et al., Atmos. Environ. 33, pp. 1423-1439 (1999)*; *B.J. Finlayson-Pitts, Chemistry of the Upper and Lower Atmosphere. Academic Press: San Diego, CA, (2000)*).

NO₃ radicals significantly contribute to the degradation of these compounds by both addition on the double bond and abstraction of the hydrogen atom from the aldehydic group (*J. Kerdouci et al., J. Phys. Chem. A 116, pp. 10135-10142 (2012)*; *M.-T. Rayez et al, J. Phys. Chem. A 118, pp. 5149-5155 (2014)*). Among the reaction products, a large part of them are organic nitrates which behave as reservoirs for reactive nitrogen and have thus an impact on ozone production.

In order to better understand the oxidation processes of unsaturated aldehydes by NO₃, a study which combines theoretical and experimental approaches has been performed for crotonaldehyde (C₄) and the ramified homologues, 2-methyl crotonaldehyde and 3-methyl crotonaldehyde in order to:

- 1) evaluate the effect of the branching on the rate constant;
- 2) determine the major pathway between the addition and the aldehydic H abstraction channels;
- 3) search for any significant activation/deactivation effect i) of the aldehydic function on the addition and ii) of the double bond on the H abstraction.

We present here the theoretical approach of the study. The 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. The results concerning geometry, vibrational analysis and energy were subsequently used to perform conventional transition state computations to predict rate coefficients and branching ratios between the various competing abstraction and addition channels. The theoretical results will be discussed and compared with the experimental findings.

38. BrHgO•: PREDICTING THE CHEMISTRY OF A PREVIOUSLY-UNKNOWN INTERMEDIATE IN ATMOSPHERIC MERCURY OXIDATION

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Abstract

Mercury is a neurotoxic pollutant that damages both human health and ecosystems, globally. Atomic mercury Hg(0) is directly emitted into the atmosphere; however, it does not readily enter the ecosystems until being oxidized to Hg(II) compounds. The oxidation of Hg(0) to Hg(II) largely limits the rate at which mercury enters the ecosystems, yet much of its mechanism remains unknown. Atomic bromine (Br•) is known to initiate Hg(0) oxidation, and BrHgONO has been identified as the major subsequent Hg(II) species. Quantum calculations indicate that photolysis of BrHgONO will rapidly produce BrHgO• (analogous to $\text{HONO} + h\nu \rightarrow \bullet\text{OH} + \text{NO}$). Although there is no experimental data on BrHgO•, it was previously computed to be thermally stable. As a result, the atmospheric fate of BrHgO• is expected to be reaction with trace gases.

We present the potential energy profiles for the reactions of BrHgO• with NO, NO₂, and a few trace organic compounds (CH₄, C₂H₆, CH₂=O, and C₂H₄) at the CCSD(T)//M06-2X level of theory. Temperature-dependent rate constants for a subset of reactions were calculated using variational transition state theory (VTST) and asymmetric Eckart tunneling. BrHgO• may efficiently abstract hydrogen atoms from alkanes and aldehydes, and our results imply that abstraction to produce BrHgOH will be a significant fate of BrHgO•.

BrHgO may also undergo addition reactions with NO, NO₂, alkenes, and aldehydes. Addition reactions with aldehydes and alkenes involve pre-reactive complexes, making it difficult to reliably calculate rate constants.

In the absence of experimental data on BrHgONO and BrHgO• kinetics, our work seeks to provide guidance for modelers and field scientists in identifying atmospheric Hg(II) compounds.

39. OH RADICAL CAN INITIATE OXIDATION OF Hg(0) IN THE UPPER TROPOSPHERE

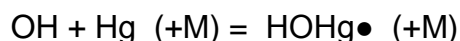
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Abstract

Modelers have expended a great deal of effort to simulate the transfer of mercury from the atmosphere to ecosystems. This transfer is largely limited by the rate of oxidation of gaseous Hg(0) to Hg(II), but many modelers use physically implausible oxidation mechanisms. Oxidation of Hg(0) by OH is described in many mechanisms as an irreversible reaction leading to gas-phase HgO, but this reaction is endothermic by ~200 kJ/mol! Here we present a mechanism for Hg(0) oxidation by OH that is physically and chemically plausible. The first step forms HOHg•, which can decompose back to OH + Hg via:



with rate constants k_1 and k_{-1} . Alternatively, HOHg• can react with a range of radicals, •Y:



(•Y = NO₂, HOO, ClO, BrO, etc.).

We obtain rate constants for all three reactions in this mechanism by combining data from four sources:

- 1) The rate constant (k_1) for OH + Hg is obtained from laboratory kinetic studies of OH reacting with Hg in the presence of large concentrations of NO₂;
- 2) The equilibrium constant for OH + Hg = HOHg• is determined by quantum calculations at very high levels of theory. In combination with k_1 , this yields the rate constant for HOHg• decomposition (k_{-1});
- 3) The similarity of HOHg-Y bonds to BrHg-Y bonds are shown by quantum chemistry calculations;
- 4) Based on item (3), we assume that rate constants for HOHg• + •Y reactions equal those known for BrHg• + •Y reactions.

The HOHg• intermediate will decompose rapidly near room temperature. Current models neglect this process, thereby grossly overestimating the efficiency by which OH initiates the oxidation of Hg(0). The present work yields a complete mechanism and set of rate constants for use in modeling the oxidation of Hg(0) by OH radical in the atmosphere.

The results imply that, near ground level in temperate and tropical regions, the main fate of HOHg• is dissociation to •OH + Hg. At the lower temperatures and pressures of the upper troposphere, HOHg• will live long enough that reaction with NO₂ and HOO can compete with dissociation.

40. RATE COEFFICIENTS FOR OH + VOC REACTIONS BY A NEW, RAPID, RELATIVE RATE TECHNIQUE

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Abstract

A large quantity and variety of volatile organic compounds (VOC) have been reported as trace gases in the atmosphere. Oxidation of these compounds by the hydroxyl radical (OH) is a crucial (often rate determining) step in atmospheric chemistry, initiating many of the processes which have impacts on air pollution and human health. Bimolecular rate coefficients for these reactions are therefore crucial parameters. However, traditional methods for rate coefficient determination are time consuming and many OH + VOC reactions have not been studied in the laboratory. Consequently, a new, self-consistent relative rate method for OH + VOC studies was developed in the York laboratories (Shaw et al., *Atmos. Chem. Phys.*, 18, 4039-4054, 2018). Rapid, simultaneous study of up to twelve reactions was a key feature of this method; more than one hundred rate coefficients were determined, with reasonable precision, in two years. In this work, room temperature rate coefficients for reactions of OH with a variety of atmospheric alkanes, alkenes and aromatics are presented. These results are discussed in the context of available literature (experimental and SAR).

41. ATMOSPHERIC OXIDATION CHEMISTRY OF METEOR ABLATED PHOSPHOROUS

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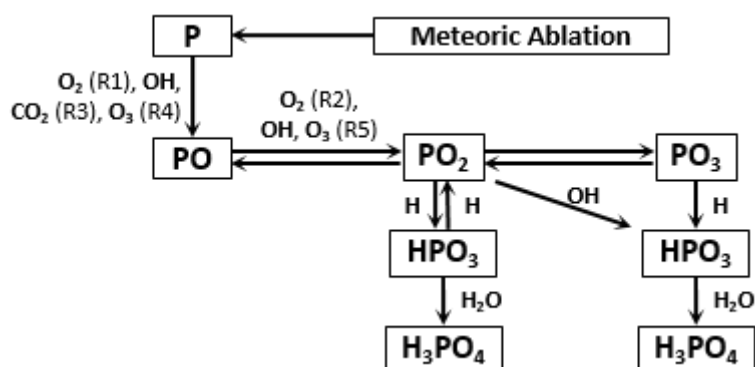
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Abstract

Phosphorous, P, is a key biological element with major roles in replication, information transfer, and metabolism. Interplanetary dust contains 0.1% P by weight, and meteoric ablation in the 1 μ bar region of a planetary upper atmosphere can generate a significant source of atomic P which will then undergo atmospheric processing before deposition at the surface. Figure 1 shows a schematic diagram of the likely chemistry in an oxidizing upper atmosphere. Using a pulsed laser photolysis (PLP)-laser induced fluorescence (LIF) technique, reactions R1 to R3 have been studied as a function of temperature for the first time, and studies of reactions R4 and R5 are currently underway. P atoms were generated in the presence of O₂ by PLP of PCl₃, and the subsequent growth and decay of the PO radical monitored by LIF in the $A^2\Sigma^+ \leftarrow X^2\Pi$ system near 247 nm. Reaction R1 shows a small negative temperature dependence, varying as $T^{-0.5}$, whereas R2 shows a small positive temperature dependence, varying as $T^{0.65}$. Reaction R1 has also been shown to have a pressure dependence, with the rate decreasing with increasing pressure. We attribute this pressure dependence to the interference of two reactive low-lying metastable states of P (the ²D and ²P), which are quenched at higher bath gas pressures. No change in rate is observed as the pressure is taken from 10 to 15 torr, suggesting the rate coefficients measured at 10 torr and above are for the reaction of ground state P (⁴S) with O₂. No pressure dependence was observed for reaction R2.



42. TEMPORAL VARIABILITY OF POLYCYCLIC AROMATIC HYDROCARBONS AND THEIR OXIDATIVE DERIVATIVES IN BEIJING, CHINA: WINTERTIME OBSERVATIONS.

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Abstract

Polycyclic Aromatic Hydrocarbons (PAHs) are known to be produced directly by combustion and are mostly emitted from anthropogenic sources; some have a strong mutagenic effect on human health. PAHs undergo reaction with oxidants in the atmosphere leading to the generation of a range of airborne nitrated-PAHs and oxygenated-PAHs, that in some cases are more toxic than the parent-PAHs.^{1,2} The formation of oxy-derivative and nitro-derivatives is influenced by local/regional emissions of PAH and oxidation rates, although relatively little is known about the variability in concentrations between daytime and night-time.

This study shows the temporal distribution of 16 particulate phase pPAHs, 11 o-PAHs and 5 n-PAHs in Beijing - China. PM_{2.5} samples were collected using a high volume air sampler (80 m³ h⁻¹) every three hours during daytime and over 15h at night-time during 18 continuous days (22 November 2016 to 9 December 2017). Fifty-seven samples in total were collected and extracted using an accelerated solvent extractor and analysed by GC-Q-ToF-MS in electron impact mode.

A range of different PAHs and o-PAHs were observed on most days, however n-PAHs were not always detectable in the 3h day samples and for some days the detection limit of the n-PAHs provides an upper estimate of possible concentrations. The total daytime concentrations during high particulate loading conditions for PAHs, o-PAHs and n-PAHs were 665, 85, and 38 ng m⁻³, respectively, concentrations which were of the order ~ 4.7, 2.9, and 2.7 times higher than average night-time values. In addition, the most abundant PAHs during polluted day were Pyrene (82.49 ng m⁻³), Fluoranthene (85.34 ng m⁻³), Chrysene (81.19 ng m⁻³) and Benzo(b)fluoranthene (119.5 ng m⁻³). 6-Nitrobenzo[a]pyrene (28.27 ng m⁻³) was the most abundant n-PAH, while 9-Fluorenone (12 ng m⁻³), 1-Pyrenecarboxaldehyde (11.45 ng m⁻³) and Benzo[a]fluorenone (16.3 ng m⁻³) were the three major o-PAHs species.

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43. A NEW ENVIRONMENTAL SIMULATION CHAMBER (CHARME) TO STUDY THE ATMOSPHERIC REACTIVITY AND THE METROLOGY OF THE ENVIRONMENT: DESIGN, CHARACTERIZATION AND PRELIMINARY TESTS

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Abstract

The most direct and significant way to examine atmospheric processes and mechanisms occurring in the atmosphere and to simplify this extremely complex physico-chemical system is to simulate atmospheric conditions in large reactors known as simulation chambers. Atmospheric simulation chambers have been used for more than 60 years and are still being constructed and developed worldwide (Finlayson-Pitts and Pitts Jr, 1999). A new simulation chamber has been developed by the LPCA (Laboratoire de Physico-Chimie de l'Atmosphère) in Dunkerque: CHARME (CHamber for the Atmospheric Reactivity and the Metrology of the Environment) which is the largest indoor chamber in France. It is an electro-polished stainless steel cylindrical reactor with a volume of 9.2 m³. The detailed characteristics of this new reactor will be presented here. The validation tests including the mixing time, the wall loss rates of gases and particulate matter (PM), the light intensity measurement (JNO₂) have been carried out to characterize the chamber's parameters. In addition, experiments were performed to study the ozonolysis reaction of some monoterpenes and the results revealed kinetic rate constants and secondary organic aerosol (SOA) yields that are in agreement with those of the literature. These tests demonstrate that CHARME chamber is valuable to provide data for gas phase chemistry, and secondary aerosol formation as well as to develop optical setups for the metrology of the atmosphere (for instance Incoherent Broadband Cavity Enhanced Absorption Spectroscopy - IBCEAS for NO₃ radicals or aerosols).

44. ATMOSPHERIC FATE OF IDOMETHANOL, UNIMOLECULAR DECOMPOSITION AND ITS REACTION WITH OH RADICALS

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Abstract

Iodomethanol is one of the atmospheric degradation product of CH₃I, which is viewed as the dominant species with the highest mixing ratio (A. Saiz-Lopez et al., Chem. Rev., 112, pp 1773-1804 (2012)). The atmospheric fate of CH₂IOH has not yet been characterized in the literature either from experimental or theoretical studies.

The main objective of this work to provide reliable kinetic and thermodynamic data for its gas phase reaction with the major photooxidant OH using high-level ab initio studies. Several reaction pathways are studied in order to assess the branching ratios: H or I atoms can be abstracted from CH₂IOH under attack of OH radicals (Fig. 1: Schematic drawing of the structures optimized at the MP2/cc-pVTZ level of theory for the I-abstraction reaction pathway. Bond lengths, bond and dihedral angles are in angstroms and degrees, respectively). As it is well known from experiments performed on fluorinated alcohols (J. Calvert, Mechanisms of Atmospheric Oxidation of the Oxygenates, Ed. Oxford (2011)), the HI elimination from CH₂IOH has been also studied.

The structures (optimized geometries and vibrational frequencies) for all stationary points on the potential energy surface are obtained at the MP2/cc-pVTZ level of theory. The potential energies have been calculated at the CCSD(T)/aug-cc-pwCVnZ (n =D, T, Q) level of theory on the geometries optimized previously. The core-valence correction is computed at the CCSD(T)/aug-cc-pwCVTZ level of theory. The scalar relativist effects are performed with the CISD/aug-cc-pVTZ level of theory.

Acknowledgments: This study takes part in the commun laboratory C³R (CNRS/IRSN/Lille). This work was part of the CaPPA project. Computer time for part of the theoretical calculations was kindly provided by Informatiques CRI Lille and the CRIANN.

45. ANALYSIS OF GAS-PHASE AND PARTICULATE REACTION PRODUCTS FROM HIGH-NO_x PHOTOOXIDATION OF n-DODECANE: INFLUENCE OF TEMPERATURE AND RELATIVE HUMIDITY ON SECONDARY ORGANIC AEROSOL FORMATION

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Abstract

Organic aerosol (OA) plays an important role in atmospheric chemistry, climate change and public health. While OA particles can be directly emitted into the atmosphere, they can also be introduced in the atmosphere by secondary organic aerosol (SOA) formation. However, our current knowledge of oxidation pathways and chemical composition of SOA is limited and poorly understood considering the difficulty of the chemical transport model to predict the OA mass in the atmosphere. It results in large uncertainties in the estimation of the impact on climate and air quality of atmospheric aerosols.

In this context, the aim of this work is to study SOA formation from oxidation of precursors such as long chain alkanes which represent a substantial fraction of the unresolved complex mixture in diesel fuel. Beside the fact that it represents a relevant class of compound for the urban atmosphere, long chain alkanes are also very interesting model-molecules to investigate the sensitivity to different reaction pathways of organic matter, i.e. fragmentation, functionalization or oligomerization, during atmospheric oxidation.

The experiments were carried out in the CESAM chamber. It is a 4,2 m³ stainless steel chamber which allows experiments to be conducted at different temperatures and relative humidities at constant pressure and under a very realistic actinic flux. It is also equipped with a large range of analytical instruments to characterize the gas-phase and particulate reaction products. In particular, the present work assesses the effect of temperature (from 10 to 30°C) and relative humidity (from <1 to 70%) on the high-NO_x photooxidation of n-dodecane. Aside from aerosol mass production, the mechanism was also investigated by measuring SOA composition. Mechanistic pathways of the gaseous and particulate products will be proposed.

This work was supported by the European Community within the 7th Framework Program, section "Support for Research Infrastructure – Integrated Infrastructure Initiative": EUROCHAMP-2 and also by the French National Programme of Atmospheric Chemistry (PN-LEFE CHAT). CNRS-INSU is acknowledged for supporting the CESAM chamber as national instrument.

46. HO₂/ACETONE CHEMISTRY: TEMPERATURE DEPENDENCE OF ACETONYLPEROXY AND CHAPERONE MECHANISM RATE CONSTANTS

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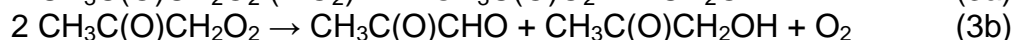
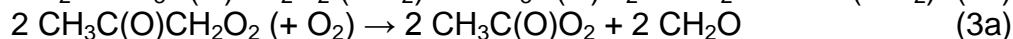
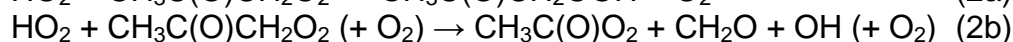
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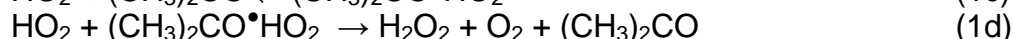
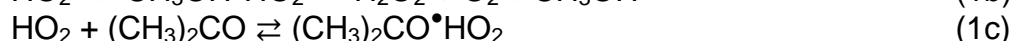
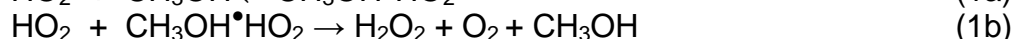
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Abstract

Building on our room temperature study (Grieman et al., AGU Fall Meeting Abstracts, 2017), the kinetics of the acetylperoxy/hydroperoxy radical chemistry has been investigated using Infrared Kinetic Spectroscopy (IRKS) from T = 230 – 300 K. In this technique, excimer laser flash photolysis of a methanol/acetone/Cl₂ mixture generates HO₂ and CH₃C(O)CH₂O₂. [HO₂] as a function of time is monitored in the infrared by diode-laser/wavelength-modulation detection and [CH₃C(O)CH₂O₂] via ultraviolet absorption at 310 nm. The rate constants for the acetylperoxy/hydroperoxy self reactions and cross reaction are determined by simultaneously fitting the decay curves to the reaction kinetics:



The fitting required including the chaperone enhancement of the HO₂ self reaction via hydrogen bonded complexes:



which must be included in laboratory studies. Given the fast equilibria (1a and 1c), the chaperone enhancement is modeled as the self reaction itself with an "observed" rate constant, $k_{1\text{obs}} = k_1 + k_1' [\text{CH}_3\text{OH}] + k_1'' [(\text{CH}_3)_2\text{CO}]$. k_1' has previously been determined (Christensen et al. J. Phys. Chem. A 2006, 110, 6948). We are then able to measure k_1'' and compare the relative magnitudes of the chaperone enhancement between the two hydrogen bonded complexes. Our method for handling the temperature dependence of the kinetics of the complex chemistry of the intermediates and products generated will be presented as well.

Surprisingly, given the importance of the acetylperoxy radical in the atmosphere, to date only one measurement of the cross reaction rate constant, and two of the acetylperoxy self reaction rate constant, have been reported, all at room temperature (Bridier et al., J. Chem. Soc. Faraday Trans. 1993, 89, 2993; Cox et al., Chem. Phys. Lett. 1990, 173, 206). We will present new room temperature values (significantly different than previously found), the chaperone enhancement parameter, and their temperature dependences.

47. REACTIVITY OF GREEN LEAF VOLATILES (GLVS) IN THE ATMOSPHERE: KINETICS, PRODUCTS AND SECONDARY ORGANIC AEROSOL FORMATION

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Abstract

In nature, plants can undergo many different stress phenomena. In response to biotic or abiotic stress factors, they will emit so-called Green Leaf Volatiles (GLVs), which are part of the large group of biogenic volatile organic compounds (BVOC). Among the BVOCs, unsaturated aldehydes are emitted in larger quantities from plants during stress periods; however, the understanding of their atmospheric reactivity is still very limited, particularly with respect to their impact on secondary organic aerosol (SOA) formation. Accordingly, the main objective of the present work is to investigate the fate of unsaturated aldehydes in the atmosphere focusing on SOA formation.

In a first part, the kinetics of the reactions of trans-2-pentenal (T2P) and trans-2-hexenal (T2H) with O₃ and Cl atoms was studied both in a Teflon chamber (0.3 m³) and in a Pyrex laminar flow reactor (O₃ only) at the SAGE department.

The second part was focused on the investigation of SOA formation during the ozonolysis of T2P and T2H in three different environmental chambers: the Teflon reactor mentioned above, the stainless steel CHARME (CHamber for Atmospheric Reactivity and Metrology of the Environment) at the LPCA (9.2 m³) and the quartz reactor QUAREC at the University of Wuppertal (1.1 m³). Parallel investigation of gaseous products by gas/liquid chromatography and IR spectroscopy was also carried out. Results will be discussed in terms of chemical mechanisms and the effect of the chamber.

48. REACTIVITY OF A SERIES OF ALKANES AND ALKENES WITH XO RADICALS (X=Cl, Br AND I): A COMPUTATIONAL STUDY

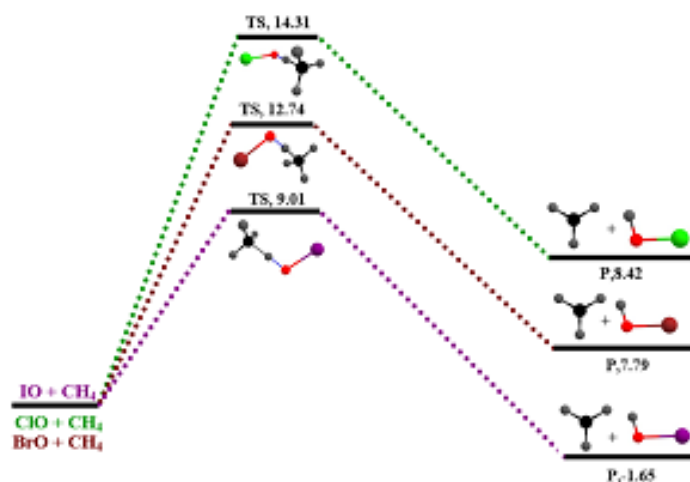
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Abstract

XO radical chemistry (X = Cl, Br and I) plays a vital role in determining the extent of ozone depletion via the generation of halogen (X) atoms (R. Vogt, P. J. Crutzen, R. Sander, *Nature*, 383, 327–330 (1996)). A major source of ClO radicals in the Earth's atmosphere is by the photolysis of chlorinated compounds, whereas the BrO (S. M. Fan, D. J. Jacob, *Nature*, 359, 522–524 (1992)) and IO (L. J. Carpenter, *Chem. Rev.*, 103, 4953–4962 (2003)) radicals are mainly emitted from oceanic and macroalgal sources respectively. In this work, we provide a comprehensive investigation on the reactivity of a series of alkanes (CH_4 , C_2H_6 , C_3H_8 and C_4H_{10}) and alkenes (C_2H_4 , C_3H_6 , and C_4H_8) with XO radicals respectively, using sophisticated computational tools. Optimized geometries for ClO, BrO and IO radicals were obtained using the M062x level of theory with 6-311++G (2df, 2p), 6-31+G (d, p) and GenECP [LanL2DZ for I atom and 6-31G (d, p) for C, H and O] basis sets respectively. Hindered-rotor corrected rate coefficients were computed using the Canonical Variational Transition State Theory (CVT) with Small-Curvature Tunneling (SCT) corrections over the entire temperature range. The reactivity of alkanes and alkenes were found to increase with the increase in the carbon number. In the case of alkanes, abstraction was found to be the only channel for their degradation. On the other hand, both addition and abstraction channels compete in the case of alkenes.



49. OH RADICAL FORMATION FROM THE REACTIONS OF OZONE WITH DIMETHYL AND TRIMETHYL AMINES

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Abstract

Organic amines released into the atmosphere are removed not only by heterogeneous uptakes on aerosols but also by gas-phase reactions with atmospheric oxidants, especially OH radical. Ozone (O_3) is also one of the important oxidizing species and can initiate the atmospheric oxidation of organic compounds containing a C=C double bond. Although alkyl amines do not contain a C=C double bond, they are known to react with O_3 . Our recent theoretical study¹⁾ suggested that the reactions proceed the H-atom abstraction from amine as an initial step rather than the formation of energy-rich amine oxide and that post-reaction intermediates with the O_3H character are formed, indicating the OH radical formation. In this study, we experimentally examined if the O_3 reactions with dimethyl amine (DMA) and trimethyl amine (TMA) lead to the formation of OH radicals.

The relative rate measurements were carried out for the reactions of O_3 with DMA and TMA in the presence and in the absence of excess amount of CO, OH radical scavenger. Ethene and propene were used as reference compounds. It was found that the slope of the plot of $\ln([amine]_0/[amine]_t)$ vs. $\ln([reference]_0/[reference]_t)$ measured in the absence of excess CO was larger than that measured in the presence of excess CO. To explain the increase of the slope, it would be required that OH radicals were formed not only from O_3 + reference alkene reaction but from O_3 + amine reaction. The OH yields for the reactions of O_3 with DMA and TMA were measured by using a relative rate method in the presence of OH tracer, 1,3,5-trimethylbenzene (TMB). The change of concentration of TMB relative to O_3 consumption was measured as a function of $[TMB]/[amine]$ ratio, and the OH yields for the O_3 + DMA and TMA were estimated to be ~0.5 and ~0.3, respectively.

Reference

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50. A NOVEL, LOW COST MATERIAL FOR AUTOMOTIVE CATALYSIS

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Abstract

Catalytic processing of vehicle exhaust emissions to reduce their impacts on air quality currently requires large quantities of expensive Platinum Group Metals (PGMs). Whilst technologies for oxidation of CO are relatively mature, new materials capable of catalysing the reduction of NO_x are needed in order to meet emissions targets. Here we present a novel, low cost material (LowCat) capable of catalysing CO oxidation and NO_x reduction simultaneously. The mechanism of action of the catalyst is investigated both computationally and experimentally to inform its real world use. The LowCat material binds O₂, which can then oxidise two equivalents of CO, NO can also be oxidised by this surface O₂, a temperature dependent process observed here above 175 °C, yielding NO₂ in the gas phase and an isolated O bound to the surface. NH₃ can bind to a neighbouring site, yielding NH₂ and OH radicals on the surface. NO can react with the NH₂ to give N₂ and H₂O, whilst a further NH₃ inserts into the bond between the OH and the surface. Reaction of a further NO, either with this bound complex or an NH₂ radical after emission of H₂O, produces further H₂O and N₂. The lone surface bound O, which is crucial to the further sequence of reactions leading to NO reduction, is also readily produced from surface reduction of NO₂ to NO. This route for producing surface O from NO₂ is active and allows reduction of NO_x even at room temperature. This mechanism is in agreement with previous results on similar catalyst surfaces, but with catalytic rates sufficient to produce reduction of NO_x in real world engines. Such an efficient, affordable catalyst capable of simultaneously oxidising CO and reducing NO_x even from cold start engines could have significant impacts on human health.

51. THEORETICAL RATE CONSTANTS FOR THE 1,4-CYCLOADDITION OF SINGLET OXYGEN ON CONJUGATED CIS-DIENES

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Abstract

Singlet molecular oxygen is formed photo-chemically in the atmosphere, e.g. via spin transfer from triplet excited molecules and photo-absorption by O₂. The lowest singlet state (singlet oxygen, ¹Δ_g) has 94 kJ/mol of energy relative to the ground state and is known to be reactive towards alkenes and sulfides. While the importance of this state has long been appreciated in other fields, for example it has been used to remove pollutants from waste water, in the photodynamic therapy for treating cancer (DeRosa, Maria C. et al., *Coordination Chemistry Reviews*, 233, pp. 351-371 (2002)) and in singlet oxygen-assisted combustion (Smirnov, V. V. et al., *Journal of Physics D: Applied Physics*, 41, 19, 192001 (2008)), it's importance in the atmosphere is not well known. Oxidation of atmospheric species are usually dominated by ozone and OH radicals, however singlet oxygen could be an important reaction path for some atmospheric species. The reactions may be especially important in fog and ice, (Anastasio, Cort, et al., *Atmospheric Environment*, 35.6, pp. 1079-1089 (2001)) and (Bower, Jonathan P. et al., *Atmospheric Environment* 75, pp. 188-195 (2013)). In-depth knowledge the kinetic parameters of singlet molecular oxygen reactions are central for evaluating the impact of ¹O₂ on the atmosphere's oxidation capacity. Gas-phase reaction rate coefficients have been experimentally determined for a small number of compounds; even fewer reactions have been investigated using quantum chemistry. This is due in part to the challenge of describing the multi-reference character of singlet oxygen. We have tested a novel and straightforward strategy to calculate rate constant for the 1,4-cycloaddition of singlet oxygen to cis-dienes and have compared the calculated rates with experimental results. The agreement between the suggested computational method and the experimental data is within one order of magnitude, to our knowledge the best that has ever been achieved. Our results open a method of evaluating the impact of reactions with singlet oxygen where experimental data is lacking.

52. OXIDATION OF ALKYL ESTERS BY OH RADICALS AND Cl ATOMS: AN EXPERIMENTAL AND COMPUTATIONAL STUDY

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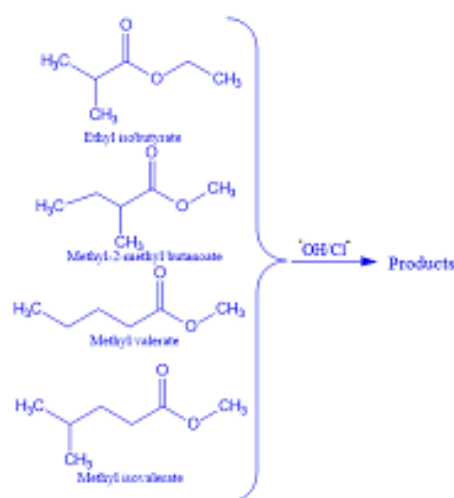
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Abstract

Oxygenated volatile organic compounds (OVOCs) are of great significance in the atmospheric chemistry. Esters are one such class of OVOCs, emitted to the troposphere via both biogenic and anthropogenic sources (A.Mellouki et al., Chem. Rev, 115, 10, 3984-4014(2015)). Moreover, alkyl esters and their corresponding radicals produced in the reaction of Cl atoms/ OH radicals were observed to be important intermediates in the pyrolysis of biodiesel (E.Jonas et al., Atmos. Environ., 44, 5407–5414 (2010)). In the present study, the gas phase kinetics of ethyl isobutyrate (EIB), methyl-2-methyl butanoate (M2MB), methyl valerate (MV) and methyl isovalerate (MIV) with OH radicals and Cl atoms were measured as a function of temperature (263-363 K) at 760 Torr using relative rate technique. C₂H₆, C₂H₄, C₃H₆, n-C₄H₁₀, i-C₄H₁₀ and C₃H₆O were used as reference compounds. The obtained rate coefficients (k, in cm³molecule⁻¹s⁻¹) at 298 K are $k_{\text{EIB}+\text{Cl}} = (6.66 \pm 0.56) \times 10^{-11}$, $k_{\text{M2MB}+\text{Cl}} = (9.54 \pm 0.41) \times 10^{-11}$, $k_{\text{MV}+\text{Cl}} = (1.72 \pm 0.21) \times 10^{-10}$, $k_{\text{MIV}+\text{Cl}} = (1.04 \pm 0.11) \times 10^{-10}$, $k_{\text{EIB}+\text{OH}} = (3.00 \pm 0.52) \times 10^{-12}$ and $k_{\text{M2MB}+\text{OH}} = (4.10 \pm 0.31) \times 10^{-11}$ respectively (I.Stefanie et al., Environ .Sci .Pollut .Res., 22,4820-4832 (2015)). Computational calculations were also performed using CVT/SCT method. The kinetic data was obtained over the temperature range of 200-1000 K. The obtained branching ratios, thermochemistry, lifetime and degradation pathways of alkyl esters will be presented in the conference.



53. ATMOSPHERIC FATE OF OXYGENATED BIOGENIC VOLATILE ORGANIC COMPOUNDS

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Abstract

Besides the known BVOCs, such as isoprene and monoterpenes, a number of oxygenated BVOCs are emitted from vegetation and have been widely observed such as C₅ and C₆ aldehydes and alcohols released by plants in response to their wounds. These BVOCs are therefore likely to have a great influence on atmospheric chemistry both locally and regionally, through their impact on the HO_x balance (HO_x = HO + HO₂), ozone production and ability to form secondary organic aerosols (SOA). Few information exists regarding the atmospheric fate of these compounds especially their reaction with ozone.

In this work, the kinetics and the mechanisms of the reaction of three unsaturated aldehydes (trans-2-pentenal, trans-2-hexenal and 2-methyl-2-pentenal) and three unsaturated alcohols (1-penten-3-ol, cis-2-penten-1-ol and trans-3-hexen-1-ol) with ozone O₃ were carried out in a rigid atmospheric simulation chamber interfaced to an FTIR spectrometer and to an SPME-GC/MS over the temperature range 273-353 K and at atmospheric pressure. The rate coefficients of the ozonolysis of the unsaturated aldehydes are of order of $2 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ while for the alcohols, they are of order of $10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Both kinetics exhibit positive temperature dependence and are influenced by their structures. This work is the first temperature dependence study for the reaction of ozone with above-mentioned alcohols and aldehydes.

Carbonyl products formation yields were measured. However, the ozonolysis of these compounds leads mainly to the formation of multi-functional compounds such as bicarbonyl, hydroxy carbonyl and carbonyl compounds. Reaction mechanisms were established. Finally the atmospheric persistence of the studied compounds is discussed. The measured rate coefficients are used to estimate tropospheric lifetimes for these compounds.

54. A KINETIC STUDY OF GAS PHASE OH RADICAL REACTION WITH 2-CHLOROETHYL VINYL ETHER USING LASER INDUCED FLUORESCENCE TECHNIQUE IN THE ATMOSPHERIC TEMPERATURE RANGE

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Abstract

Alkyl vinyl ethers, ROCH=CH₂, are class of compounds which have C=C group and etheric oxygen (O) in immediate proximity. 2-Chloroethyl vinyl ether (2CLEVE) is halogenated vinyl ether, in which one H atom in the alkyl group is replaced by Cl atom. It has many industrial uses starting from the manufacturing of cellulose ethers, anaesthetics and sedatives, and also as a precursor of polymers (E. Mechref et al., RSC Adv., 6 pp. 3951–3959 (2016), H. Boucekif et al., Polym. Chem., 6 pp. 1236–1247 (2015), M. Chabani et al., J. Appl. Polym. Sci, 122 pp. 1800–1806 (2011)). Due to its extensive use, 2CIEVE is emitted into the atmosphere. Therefore, it is important to determine its reaction rate with OH radical, which is most abundant oxidative species in the troposphere. It is also desirable to estimate its tropospheric lifetime and global warming potential. The title reaction was previously studied using relative rate method (S. Peirone et al., Atmos. Envir., 45 pp. 5325–5331 (2011)) and absolute rate method (M. Antiñolo et al., Chemosphere, 181 pp. 232–240 (2017)), however, there was discrepancy in reported rate coefficient value at room temperature. In this context, we have undertaken this present study to evaluate the rate coefficient for OH+2CIEVE reaction and discuss the origin of the discrepancies.

In this work, the absolute rate coefficient for the gas phase reaction of OH radical with 2CIEVE had been measured using the laser photolysis (LP) laser induced fluorescence (LIF) technique. The kinetics measurements were done over the tropospheric temperature range of 256–333 K. The bimolecular rate coefficients obtained, $k(T)$, are pressure independent in the range of 20–40 Torr and shows Arrhenius type behaviour, which are fitted to the expression $k(T)=(4.18\pm 0.55)\times 10^{-12}\exp[(700\pm 70)/T]\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$. The reaction shows weak negative temperature dependence. Along with these experimental studies, theoretical calculations were also carried out to understand the mechanism of OH radical addition to C=C bond and abstraction mechanism of H atom using mainly using the Gaussian programs (M. Frisch et al., Gaussian 03, Pittsburgh PA, (2003))

55. NEW OBSERVED TRIPLE FRAGMENTATION PHOTOLYTIC PATHWAY OF PROPANAL

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Abstract

Aldehydes and ketones are important trace components in the atmosphere, both as direct emissions and from oxidation of other species. The photochemistry of these compounds plays a significant role in atmospheric chemistry, producing radicals which then can react with other species. The two smallest atmospheric aldehydes, H₂CO and CH₃CHO have been well-studied. The next largest, propanal, is much less studied, even though it is reported to be one of the most abundant aldehydes in the emission of biofuels ¹⁻³. Additionally, propanal provides a good case study to determine whether the photochemical pathways prevalent in the two smaller species are equally relevant in larger aldehydes, more generally.

Photodecomposition of all carbonyl compounds via well-known Norrish type I reaction NT(I) R-CO-R' RCO + R' is one of the major sources of free radicals where R and R' represent alkyl groups for a ketone and include the H-atom for an aldehyde. In propanal, this pathway is also considered to be the dominant photolytic channel under atmospheric conditions. However, the absolute quantum yield of NT(I) reaction from two different available experimental reports were reviewed by Atkinson and suggested to be inconsistent ⁴.

Moreover, recent discovery of keto-enol phototautomerization on the ground state electronic of acetaldehyde have demonstrated the importance of ground state reaction pathways⁵. Theory demonstrates that there are other ground photodissociation channels in propanal that are energetically available in the actinic region, such as channels to H₂+methylketene and triple products CO+H₂+C₂H₄. These pathways have not been experimentally observed previously, nor considered in atmospheric chemistry models.

In this work we explore the photochemical pathways of propanal by investigating wavelength and pressure-dependent photochemistry of this molecule in the 300 - 330 nm region using laser photolysis and FTIR detection of stable products. We find that our NTI quantum yields are in good agreement with one of the two previous sets of data. We also find that triple fragmentation occurs with a quantum yield of 2-4% and no evidence for photo-tautomerization.

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56. AB INITIO INVESTIGATION OF THERMOCHEMICAL PROPERTIES OF VERY-SHORT LIVED BROMINATED SUBSTANCES (VSLS)

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Abstract

Bromine atoms are very efficient catalysts in destroying stratospheric ozone. Very-short lived brominated substances are an important source of stratospheric bromine. Modelling of the atmospheric chemistry of brominated hydrocarbons requires reliable thermochemical data.

The aim of this work is to build a thermochemical database for brominated organic species. The inclusion of the obtained parameters in atmospheric models will help to further improve our understanding of their atmospheric impacts. In addition, the new thermochemical data can be included in low temperature (< 1000 K) detailed combustion mechanisms of brominated organic compounds in which alkylperoxy radicals play a significant role.

In this work, we investigate the thermochemical properties of halogenated species such as ROO and RO (R = CH₂Br, CHBr₂, CBr₃) in their atmospheric degradation pathways using our new estimation of the standard enthalpies of formation at 0 and 298 K of the following species: CH₃OO, CH₃O, CH₃OH, and CH₃OOH. Optimized structures and vibrational frequencies were computed at the MP2/aug-cc-pVTZ level of theory. To obtain more accurate electronic energies, single-point energy calculations were performed for MP2 geometries using coupled cluster theory (CCSD(T)) and the weighted core-valence basis sets aug-cc-pwCVnZ (n = T, Q, 5). Core-valence calculations were carried out at the CCSD(T)/awCVTZ level of theory. The scalar relativistic corrections were computed at the CISD/aVTZ level of theory. The spin-orbit coupling was evaluated at the MRCI/aug-cc-pVTZ level of theory.

Acknowledgments: This work was part of the CaPPA project (Chemical and Physical Properties of the Atmosphere). Computer time for part of the theoretical calculations was kindly provided by CRI Lille and CRIANN. We thank the Slovak Research and Development Agency (Project APVV-15-0105) for support.

57. DEVELOPMENT AND VALIDATION OF A NEW EXPERIMENTAL SET-UP TO STUDY REACTIONS BETWEEN RO₂ AND HO_x RADICALS

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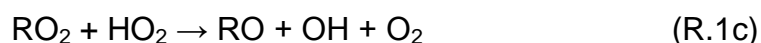
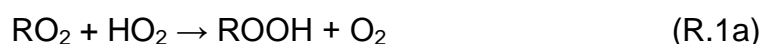
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Abstract

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 such as hydroperoxy HO₂ and alkylperoxy RO₂, which play a major role in tropospheric chemistry. The reactivity of these 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 NO_x concentrations (remote regions: marine boundary layer or tropical forest).

The reaction between RO₂ and HO₂ radicals can lead to termination (R.1a: radicals sink) or propagation (R.1c: formation of new OH radicals) pathways:



If reactions with simple alkylperoxy radicals (R= CH₃, C₂H₅) are well known, significant disparities appear in the literature for more complex RO₂ radicals. Moreover, very recently, a new reaction pathway has been suggested as possible fate of RO₂ radicals in clean environments: the reaction with OH radicals. Only few studies exist on this class of reactions and to date, they are not included in atmospheric chemistry models. Then, there is clearly a need for new experimental studies of RO₂ + HO_x (OH, HO₂) reactions to improve our knowledge of this class of reactions and their atmospheric implication.

The aim of the present work is the development of a new experimental device to study reactions between RO₂ and HO_x (rate constants and branching ratios measurements). The new setup consists of a fast flow tube (10-30 m.s⁻¹) coupled to three complementary techniques:

- Laser Induced Fluorescence (LIF) for in-situ OH radicals measurement
- continuous wave Cavity Ring-Down Spectroscopy (cw-CRDS) for HO₂ radicals measurement
- Mass Spectrometry with Molecular Beam sampling (MB/MS) for measurement of stable reaction products and radical species

We will present the validation of each individual technique and of the overall system through the study of different reactions between alkanes (ethane, propane) + OH, alcohol (methanol) + OH and CO + OH.

58. KINETIC INVESTIGATIONS FOR GAS PHASE REACTIONS OF MONOCHLORINATED PROPANES WITH CL ATOMS: EXPERIMENTAL AND COMPUTATIONAL STUDIES.

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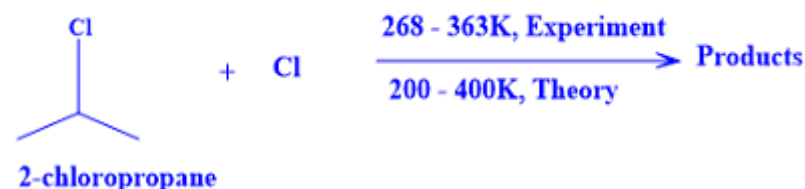
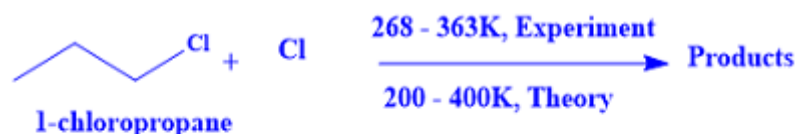
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Abstract

The reactions of Cl atoms with halogenated hydrocarbons are important to understand the chemistry of troposphere (J. Finlayson-Pitts et al., Adv. Environ. Sci. Technol., 7, pp. 75 - 81 (1987)). Photo-oxidation is an important tropospheric sink for organic compounds and it is dominated by reactions with OH radicals and Cl atoms (D. G. Hendry et al., EPA-560/12-79-001, June (1979)). Halogen-containing molecules have been extensively used in industrial as well as in domestic applications. However, anthropogenic release of these compounds into the environment can cause adverse effects such as stratospheric ozone depletion. Thus, it is necessary to study the fate of these compounds in the atmosphere.

Temperature dependent rate coefficients were measured for the reactions of 1-chloropropane(1-CP) and 2-chloropropane (2-CP) with Cl atoms over the temperature range of 268-363K by using relative rate technique. Measured rate coefficients were used to fit the Arrhenius equations and are $k(1\text{-CP}+\text{Cl}) = (2.69 \pm 1.80) \times 10^{-20} T^{3.01} \exp\{(1227 \pm 620)/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(2\text{-CP}+\text{Cl}) = (2.69 \pm 1.80) \times 10^{-20} T^{2.92} \exp\{(1227 \pm 620)/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. To complement our experimental results, computational calculations were performed in the temperature range of 200-400K for the title reaction using CVT/SCT at CCSD/cc-pVDZ//MP2/6-31+G(d,p) level of theory. In-detail studies will be discussed in the conference.



59. CONTRASTING PATHWAYS TO IODINE OXIDE PARTICLE FORMATION IN THE PRESENCE AND ABSENCE OF WATER

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Abstract

Recent experiments conducted at the University of Leeds find that the mechanism of Iodine oxide Particle (IOP) formation is significantly perturbed by the presence of atmospherically relevant concentrations of water vapour. Time-Resolved Photolysis Time Of Flight Mass Spectrometry is employed to measure the time-evolution of Iodine Oxide species formed from Pulsed Laser Photolysis (PLP) of Ozone in the presence of I₂. In the absence of water, IOP formation proceeds via disproportionation of I₂O₄ to I₃O₇ and IO, and the subsequent disproportionation of I₃O₇ to I₅O₁₂, the mechanism of which is reasonably well understood (Saiz-Lopez 2014, Gómez Martín 2013).

Upon the addition of water (~1%), the aforementioned “dry” route to IOP formation is seemingly perturbed: peak concentrations of key higher iodine oxides are significantly reduced, and the removal of key I_xO_y species appears to experience an enhancement effect from water both at low (~10 torr) and high (~500 torr) pressures. The reaction of iodine oxides under high RH conditions appears to favour formation of oxyacids such as HOI, which is observed with higher relative abundance than under dry conditions in both the high and low-pressure regimes. HOIO₂ has also been detected in these experiments under the high-pressure regime, which suggests IOP formation could proceed via oxyacid species under atmospherically relevant conditions. Further work is required to fully understand this novel chemistry, and the impact these reactions could have on the mechanism of IOP formation in the atmosphere.

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60. SO₂-CRIEGEE INTERMEDIATE REACTION'S ROLE IN THE FORMATION OF SECONDARY ORGANIC AEROSOLS

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Abstract

One of the main sources of ultrafine particles is the formation of secondary organic aerosols (SOA) from the reactions of gas-phase pollutants. Styrene was identified as the second most efficient species forming SOA (Sun et al., Atmos Environ, 141, pp. 560-570 (2016)). The reactions of alkenes with ozone proceed through the formation of Criegee Intermediates, which can undergo reactions with SO₂, producing SO₃, contributing to the formation of sulfuric acid (Mauldin et al., Nature, 488, pp. 193-196 (2012)). The reaction with SO₂ could be the key to explain the high SOA formation potential of styrene under polluted conditions. The competition of SO₂ and water vapour in the removal of sCI in the atmosphere depends on the CI structure (Díaz-de-Mera et al., Atmos Chem Phys, 17(3), 2347-2357 (2017)).

The reaction has been carried out in a Teflon chamber filled with synthetic air mixtures at atmospheric pressure and room temperature. The ozone was generated in-situ and measured by UV-vis technique. The concentration of particles was monitored by a Scanning Mobility Particle Sizer with a Condensation Particle Sizer in the 4.0-150 nm size range. A series of experiments was carried out to characterize the nucleation threshold. The ozonolysis of styrene produces new particles in the presence of low concentrations of SO₂, at reacted reagents concentrations around $(5.6 \pm 1.7) \times 10^8$ molecule cm⁻³.

We have assessed the effect of the variation of styrene and ozone reagents as well as the addition of SO₂ and/or water. The fractional yields for different initial concentrations of reactants are independent on the concentrations of styrene or ozone but increase from nearly zero in the absence of SO₂ to approximately 2 when SO₂ is in excess.

The experimental temporal decays of SO₂ show that it reacts with the products of the ozonolysis of styrene. From the profiles of reacted styrene, the yield for the consumption of SO₂ was $\eta = 0.51 \pm 0.13$. Thus, the formation of SO₃ from the reaction of styrene with the CI is expected to be responsible of the nucleation events through the formation of H₂SO₄. On the other hand, the presence of water in the reaction media competes with SO₂ and inhibits the formation of SOA. So the potential formation of SOA under atmospheric conditions depends on the concentration of SO₂ and relative humidity, with $k_{\text{H}_2\text{O}}/k_{\text{SO}_2} = (2.8 \pm 0.7) \times 10^{-5}$.

61. ATMOSPHERIC SINKS OF STYRENE: RATE COEFFICIENT AND MECHANISM OF THE Cl ATOMS INITIATED DEGRADATION.

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Abstract

Styrene is an aromatic compound that can be emitted into the atmosphere from different sources such as solvents, combustion (i.e., gasoline and diesel engines), building materials and industrial processes (Knighton et al., *Ind Eng Chem Res* 51, 12706-12711 (2012)). Styrene is considered an important secondary organic aerosol (SOA) precursor (Diaz de Mera et al., *Atmos Environ*, 171, 25-31 (2017)) and a primary contributor to photochemical ozone formation (Berezina et al., *Dokl Earth Sci*, 474, 599-603 (2017)).

Styrene can be removed from the atmosphere via reactions with OH radicals during the daytime, NO₃ radicals at night, O³ during both day and night, Cl atoms at dawn (Atkinson and Arey, *Chem Rev*, 103, 4605-4638 (2003)) or undergo direct photolysis. To the best of our knowledge, this is the first report of the identification of products for the reaction of the Cl atoms with styrene, only the rate constant has been studied previously (Shi and Bernhard, *Int J Chem Kinet*, 29, 349-358 (1997)).

Kinetic experiments were carried out in a 400 L Teflon reaction chamber using GC-FID for the analysis, and products were determined using a 56 L quartz-glass reactor coupled to a FTIR spectrophotometer. The rate constants at 298 K was $(1.42 \pm 0.30) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (errors are 2σ), which is not in agreement with the value determined by Shi and Bernhard (Shi and Bernhard, *Int J Chem Kinet*, 29, 349-358 (1997)), $(3.6 \pm 0.3) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The identification of benzaldehyde, formyl chloride and formaldehyde is consistent with Cl-addition to the double bond of the vinyl group, with molar yields of $(24 \pm 3)\%$, $(24 \pm 4)\%$ and $(30 \pm 2)\%$, respectively.

In order to evaluate the atmospheric importance of a particular reaction, it is also necessary to consider the reaction mechanism and the product formation, so styrene will undergo rapid degradation in the troposphere giving carbonyl compounds, which also play an important role in the atmosphere due to their involvement in photochemical reactions and contribution to aerosol particle formation and growth (Jang and Kamens, *Environ Sci Technol*, 35, 4758-4766 (2001)) and HCOCl, which is expected to be incorporated into rain, clouds and fog water followed by hydrolysis and removal by wet deposition (Wallington, et al., *Environ Sci Technol*, 28, 320A-326A (1994)).

62. DIRECT STUDIES OF CRIEGEE INTERMEDIATE REACTIONS USING CAVITY RING-DOWN SPECTROSCOPY

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Abstract

Criegee intermediates are important reactive intermediates formed during the ozonolysis of alkenes in the atmosphere. Ozonolysis is an exothermic process which breaks the alkene double bond and leads to formation of internally hot Criegee intermediates. Under atmospheric conditions, some fraction of the hot Criegee intermediates is stabilized, which can then undergo bimolecular reactions with H₂O, (H₂O)₂ and various trace atmospheric species like SO₂, NO₂ and RCOOH. Recent direct studies have shown that the rate coefficients for these reactions are fast and thus could be important in tropospheric chemistry.¹⁻⁴ Results obtained from our recent measurements of Criegee intermediate reaction kinetics using Cavity Ringdown Spectroscopy will be presented.⁵⁻⁸ Significant structural effects were observed in the bimolecular reactions of the simplest Criegee Intermediate CH₂OO and (CH₃)₂COO. In the case of Criegee + Criegee, Criegee + SO₂ and Criegee + RCOOH reactions, there are no significant chemical barriers and the reaction rate is controlled by dipole-dipole attraction. The structures of Criegee intermediates and RCOOHs significantly affect their dipole moments. For Criegee + ROH reactions, substitution about the Criegee intermediate is found to have a strong influence over reaction rate, whereas substitution on the alcohol moiety does not.⁷ In the case of Criegee + NH₃/amine, methyl substitution on both Criegee and amine significantly changes the reaction rate. Preliminary results on the Criegee + RO₂ reactions will also be presented. Structure-activity relationships obtained from these observations can be used to predict rate coefficients for the reactions of biogenic Criegee intermediates which are difficult to measure but are important parameters in global atmospheric models.

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63. CH₂OO CRIGEEE INTERMEDIATE UV ABSORPTION CROSS-SECTIONS AND SELF-REACTION KINETICS

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Abstract

The chemistry of Criegee intermediates, produced in the oxidation of unsaturated volatile organic compounds by ozone, has potentially important impacts on atmospheric composition and thus on air quality and climate. In recent years, there have been significant advances in our understanding of the properties and chemistry of Criegee intermediates following the advent of photolytic sources for use in laboratory experiments.

Measurements of Criegee intermediate UV absorption cross-sections have indicated that the absorption cross-sections are relatively large, on the order of $\sim 10^{-17}$ cm² (1-4), making UV absorption spectroscopy a useful tool for the measurement of atmospherically relevant reaction kinetics. However, for the simplest Criegee intermediate, CH₂OO, there are significant uncertainties in the UV absorption cross-sections and in the shape of the spectrum. Significant uncertainties have also been reported in the rate coefficients for the CH₂OO + CH₂OO self-reaction (5-8), the kinetics of which can be closely coupled to the determination of the absorption cross-sections since significant changes in concentration can occur on the timescale of the absorption measurements.

In this work, we report measurements of the CH₂OO UV absorption cross-sections and self-reaction kinetics made at pressures between 6 and 300 Torr using laser flash photolysis of CH₂I₂/O₂/N₂ gas mixtures coupled with time-resolved broadband UV absorption spectroscopy. Preliminary results indicate a peak absorption cross-section of $(1.4 \pm 0.3) \times 10^{-17}$ cm² molecule⁻¹ at 340 nm, and a pressure-independent rate coefficient of $(8.0 \pm 0.8) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ for the CH₂OO self-reaction. Implications of these results will be discussed.

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64. ALKOXY RADICAL BOND SCISSIONS EXPLAIN THE ANOMALOUSLY LOW SECONDARY ORGANIC AEROSOL AND ORGANONITRATE YIELDS FROM α -PINENE + NO₃

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Abstract

Biogenic emission of monoterpenes is an important contributor to the formation of secondary organic aerosol (SOA) playing a key role for the Earth's climate and with known adverse effects for human health. However, the SOA yield of different monoterpenes can be very different. For example, experiments have shown that the aerosol yield from the oxidation of α -pinene and Δ^3 -carene by NO₃ is very different despite their very similar chemical structure: While α -pinene produces very little aerosol, the yield from Δ^3 -carene is significant.

Using a combined theoretical and experimental approach, we explore the mechanisms of their individual oxidations by NO₃ to explain this disparity (T. Kurtén et al., JPCL, 8, pp. 2826-2834 (2017)). We find that even under HO₂-dominated conditions, both oxidation pathways lead to the formation of β -nitroxy alkoxy radicals in large yields. The experimentally observed difference in SOA yield is explained by the relative favorability of the two possible ring-breaking reactions for these alkoxy radicals. α -pinene breaks almost exclusively to form the closed-shell pinonaldehyde with loss of NO₂. Δ^3 -Carene, on the other hand, has an equally favorable pathway retaining the radical character and nitrate group, which may react further to form highly-oxidized compounds susceptible to partitioning into the aerosol phase

65. EXPERIMENTAL STUDY OF PHOTSENSITIZED REDUCTION OF NITROGEN DIOXIDE ON CORN AS A SOURCE OF NITROUS ACID

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Abstract

During the last decades, many studies showed an important formation of nitrous acid (HONO) by heterogeneous reaction between nitrogen dioxide (NO₂) and surfaces (soil, glasses...). During daytime, HONO is photolysed in hydroxyl radical (OH). As this compound is the principal atmospheric oxidant, it's necessary to identify and quantify the various sources of HONO. Many field measurement campaigns have reported unusually high concentrations during daytime in semi-urban and urban regions. One source of HONO is the reaction between NO₂ and soils but this reaction isn't sufficient to explain these high concentrations. One hypothesis is the formation of nitrous acid by heterogeneous reaction between NO₂ and plants. Indeed, plants represent a potential source of HONO because of their important vegetable surface in the world.

Here, we studied the formation of HONO on corn unstressed leaves and the impact of different parameters on this formation. Experiments were carried out in a flow tube reactor coupled with NO_x analyser for NO₂ and NO detection and Long Path Absorption Photometer (LOPAP) for HONO detection. In this case, temperature, relative humidity and light dependence were studied. For all experiments, NO₂ consumption, NO and HONO formations have been investigated. In all experiments, we observe NO₂ consumption and NO and HONO formation.

In view of the results obtained, relative humidity has no impact on consumption and on formation products. For temperature, an important increase of HONO formation was observed, factor five between 288 and 313K. For light parameter, an increase of NO formation was observed, factor four. For most experiments, all NO₂ consumed was converted in NO and HONO.

Others studies will be realized on water stress corn in the reactor and in growth chamber to simulate a realistic environment. These results will be used to improve prediction models for HONO formation.

66. PHOTOCATALYTIC PAINTS: IMPROVING A NEW BINDER TO REDUCE VOCS EMISSION

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Abstract

Indoor air quality has an important impact on human health. We spend over 80% of our time in indoor environment. To improve indoor and outdoor air quality, photocatalytic materials have been developed with different nanoparticles like TiO₂. These photo-catalysts, activated by UV light (<390nm), are able to oxidize atmospheric pollutants and potentially destroy harmful VOC's. In this study, the objective is to determine the surface emission rate for different compounds released by decomposition of paint binder and compare this emission for different type of paints. We tested photo and no photocatalytic paints with different matrixes aimed for indoor air application.

Experiments were performed in a flow tube reactor using a Proton Transfer Reaction-Mass Spectrometer for detection the 18 different VOC's concentrations at 298 K and RH = 40%. VOC's emission was studied for 9 different paints: 5 photocatalytic paints and 4 reference paints.

Under light irradiation, surface emission rates of all reference paints are similar but significate differences are observed for photocatalytic paints. This means that nano-TiO₂ reacts differently with the matrix. In this case, we observe an important decrease for the formation of formaldehyde, of a factor 5, with mineral matrix and a light diminution, 30-70%, with organic matrix. For the three organic matrixes, the emission rate for all compounds is similar so in this case the composition of the matrix has no impact on the emission rate. Moreover, we observe a light diminution of acetaldehyde production, 15%, with mineral paint but an increase for acrolein, 24-55%. For benzene, the emission rate is the same with the different matrixes but the emission is very low, close to the LOD of PTR-MS. In addition, a significant drop of emission rate for Butyric Acid and Methyl Vinyl Ketone has been observed with the mineral paint. This drop of emission is due to a low concentration of organic compounds in the mineral paint.

In these studies, we observed an important difference between the matrices. The mineral paint emits low concentrations compared to other paints. This information is very important for the future of photocatalytic paint development. It's necessary to make other studies with mineral matrices to measure the emission rate with different compositions and nanoparticles and find the best paint to improve indoor air quality.

67. MECHANISTIC STUDY OF THE REACTION OF CH₂F₂ WITH CL ATOMS IN THE ABSENCE AND PRESENCE OF CH₄ OR C₂H₆: DECOMPOSITION OF CHF₂OH AND FATE OF THE CHF₂O RADICAL

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Abstract

Chlorofluorocarbons (CFCs) have had several different uses (e.g. refrigeration and foam blowing). In recognition of their ability to deplete stratospheric ozone and potency as greenhouse gases (M.J. Molina and F.S. Rowland, *Nature*, 249, p. 810-812 (1974); J.C. Farman et al., *Nature*, 315, p. 207-210 (1985)), they were replaced by hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) that have smaller environmental impacts. However, they are potent greenhouse gases like the CFCs with long atmospheric lifetimes. Therefore, they are being replaced by more reactive species; e.g. hydrofluoroethers and hydrofluoroolefins. Persistent organic acids can be formed during the atmospheric degradation of halogenated species, such as the CFCs and their replacement compounds. Fluorinated peroxy radicals reacting with other peroxy radicals can lead to the formation of fluorinated alcohols (D.A. Ellis, et al., *Environ.Sci.Tech.*, 38, p. 3316-3321 (2004)). These alcohols react to form carbonyl products that can hydrolyse forming acids. Fluorinated acids in the environment is a concern for human and animal health, being toxic and likely carcinogenic as well as being bioaccumulative and biomagnifying.

FTIR chamber experiments were performed at Copenhagen Center for Atmospheric Research and Ford Motor Company investigating the degradation of CH₂F₂ as a model of an HFC. The reactions mixtures contained CH₂F₂ and Cl₂ in the absence and presence of CH₄ or C₂H₆ in a total of 700 Torr of N₂/O₂ diluents at 296 ± 2 K. Cl atoms will initiate the reactions by H atom abstraction from CH₂F₂, CH₄, and C₂H₆, following reaction with O₂ to form CHF₂O₂, CH₃O₂, and CH₃CH₂O₂. No evidence of the reaction of CHF₂O₂ with either CH₃O₂ or CH₃CH₂O₂ to give CHF₂OH was observed, but evidence of an alkoxy radical pathway was observed to be the most likely pathway forming the alcohol (with initial high concentrations of CH₂F₂). The decomposition of CHF₂OH was investigated, determining the rate of decomposition and half-life of the alcohol. CHF₂OH and HC(O)F were observed as evidence of CHF₂OH; HC(O)F being formed in the degradation of the alcohol. The competition between the reaction of CHF₂O radicals with O₂ and with CH₂F₂ was investigated and the ratio of the rate coefficients was determined. The atmospheric impact of the results is discussed.

68. STEADY STATE CONTINUOUS FLOW CHAMBER FOR THE STUDY OF ATMOSPHERIC HYDROCARBON OXIDATION CHEMISTRY UNDER DAYTIME AND NIGHTTIME CONDITIONS – CHAMBER CHARACTERIZATION AND FIRST RESULTS

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Abstract

We present here the development and characterization of the NCAR Atmospheric Simulation Chamber, a 10 m³ Teflon chamber that can be operated in a continuous flow mode that accurately represents tropospheric oxidant concentrations in either daytime or nighttime conditions. Steady-state “daytime” conditions are obtained by photolysis of an OH precursor (H₂O₂), which is continuously flowing into the chamber along with NO and the VOC under study (with constant sampling out of the chamber). This allows chemistry to be studied at controlled and constant levels of NO (about 100 ppt – 10 ppb) where peroxy radical lifetimes can be increased to approx. 1 min, allowing diverse reaction pathways including unimolecular processes and bimolecular reactions to be explored. Similarly, nighttime conditions can be achieved by continuous flow of NO and O₃ into the chamber, producing steady-state levels of NO₃ in the presence of sub-ppb levels of NO. In this presentation, an overview of the chamber capability is presented, along with some preliminary results from ‘proof-of-concept’ experiments involving both daytime (OH) and nighttime (NO₃) isoprene oxidation. In particular, yields of methylvinyl ketone and methacrolein from OH-initiated oxidation are presented over a range of peroxy radical lifetimes and compared with recently constructed chemical mechanisms.

69. TIME-RESOLVED BROADBAND CAVITY-ENHANCED ABSORPTION SPECTROMETER FOR REACTION KINETIC STUDIES OF STABILIZED CRIEGEE INTERMEDIATES

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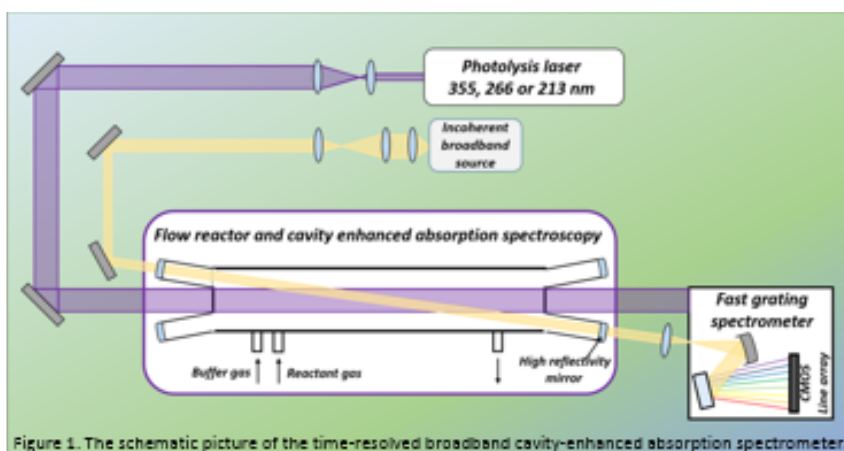
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Abstract

Stabilized Criegee intermediates (sCIs) are formed in the Earth's atmosphere as a product of ozonolysis of alkenes and have an impact on the atmospheric chemistry. These intermediates can react onward with atmospheric constituents, e.g., SO₂, NO₂, and H₂O. Stabilized Criegee intermediates can be produced reliably for the direct kinetic gas phase studies by a laser photolysis of a diiodo-compound (e.g., CH₂I₂) in the presence of O₂ (O. Welz et al., Science, 335, pp. 204 – 207 (2012)).

Here we present the design and preliminary results of a time-resolved broadband cavity-enhanced absorption spectrometer (TR-BB-CEAS) that has been designed for direct investigations of temperature-dependent sCI reactions in the UV region. The design of our TR-BB-CEAS is modified version of the experimental setup developed by L. Sheps (L. Sheps, J. Phys. Chem. Lett. B, 4, 4201 – 4205 (2013)) and its schematic picture is presented in Fig. 1. The Criegee intermediates are produced along a heated or cooled quartz flow tube reactor by a single pass photolysis laser pulse. A moderate-finesse optical cavity for the overlapping incoherent broadband probe beam enhances the detection sensitivity of the formed sCI. The time-dependent broadband absorption spectrum of sCI is measured by a grating spectrometer combined with a fast CMOS line array camera.



71. MECHANISMS FOR ATMOSPHERIC CHEMISTRY: GENERATION, INTERPRETATION AND FIDELITY - MAGNIFY

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Abstract

Over the past decade the **Master Chemical Mechanism** (<http://mcm.leeds.ac.uk/MCM>) has been hugely influential on the atmospheric chemistry community, where it is extensively used in a wide variety of science/policy applications where chemical detail is required to assess issues related to air quality and atmospheric composition. The joint UK/French MAGNIFY Project provides a strategic framework for the sustainable development of the MCM into the future. This involves a complete overhaul of its construction rules so that future generations can be auto-generated using the GECKO-A framework (Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere (<http://geckoa.lisa.u-pec.fr>)), and opening it up more to community. Detailed updates include areas such as the ozonolysis of organic species and the chemistry of the resultant Criegee intermediates, photolysis and the chemistry of polyfunctional compounds. MAGNIFY builds upon the success of the MCM, maintaining it as the “gold standard” benchmark mechanism for atmospheric chemistry.

72. ACETYLPEROXY RADICAL REVISITED - SPECTRA, ABSORPTION CROSS SECTIONS AND KINETICS OF THE SELFREACTION

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Abstract

Acetylperoxy radicals (CH_3COO_2) play an important role in the troposphere [1, 2]. They are formed in the photooxidation of carbonyl compounds, for example acetaldehyde or acetone. Whereas in clean environments they react with other organic peroxy (RO_2) radicals and hydroperoxy (HO_2) radicals, in the polluted troposphere they react with mainly NO or form peroxyacetyl nitrate (PAN) in the reaction with NO_2 .

Here acetylperoxy radicals were detected with cavity ring-down spectroscopy (CRDS) in the near infrared region. The spectra were measured in the range of 1524-1545 nm and 1618-1641 nm and show a good agreement with spectra previously published by Zalyubovsky et al. [3]. The spectrum exhibits a maximum at 1535.925 nm with an absorption cross section of $\sigma = 5.44 \times 10^{-20} \text{ cm}^2$. This absorption line was used to detect acetylperoxy radicals in kinetic studies.

Radicals were generated by photolysing Cl_2 mixed with acetaldehyde in synthetic air at 248 nm, resulting in radical concentrations of $(0.5 \text{ to } 3.5) \times 10^{13} \text{ molecules cm}^{-3}$. All experiments were performed at 298 K and 50 Torr total pressure. In addition to CH_3COO_2 , HO_2 , methylperoxy (CH_3O_2) and OH radicals were measured by CRDS. This setup allowed investigating the CH_3COO_2 self-reaction.

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73. DEVELOPMENT AND VALIDATION OF A THERMAL REGULATED ATMOSPHERIC SIMULATION CHAMBER (THALAMOS)

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Abstract

Environmental chambers, also known as atmospheric or smog chambers, are unique tools for investigating crucial atmospheric processes in the gas and heterogeneous phases; they are supposed to provide a controlled but realistic environment, aiming at simulating atmospheric conditions without any meteorological or emissive impact that occurs in the real atmosphere. Since the development of the first environmental chambers, back in the mid-1980s, several small to large-scale facilities have been developed worldwide.

Along the past 4 decades, environmental chambers have been widely used to study (i) gas phase reactions, from kinetics and reaction pathway point of view, (ii) secondary organic aerosol (SOA) formation, and (iii) nucleation phenomena, etc. Nevertheless, till today, most of the studies in smog chambers have been conducted close to ambient temperature and dry conditions, although T and RH are crucial parameters that can deeply influence the physicochemical phenomena.

In the framework of the current study we initiated activities related to the construction of a medium size Teflon atmospheric simulation chamber, named THALAMOS (THERMAL regulated AtMOSpheric simulation chamber), that can be operated in a wide temperature range (-40 to 100 C). THALAMOS is a unique experimental tool aiming at simulating both extreme outdoor and indoor processes and provide kinetic and mechanistic information about the degradation of VOCs from the major oxidants of the outdoor/indoor atmosphere. To the best of our knowledge THALAMOS is the unique facility in national level that can be operated in this wide temperature range.

To widen the general objective, the photo-oxidation (kinetics and end product analysis) of aromatic hydrocarbons (i.e. toluene, ethyl benzene, and styrene) from Cl atoms was studied. The selected aromatic probe molecules are released into the atmosphere mainly due to anthropogenic activities (cars, solvent use, industrial activities, etc.). In coastal areas, the degradation of these aromatic hydrocarbons from Cl atoms can be an important process (given the high concentration levels of Cl atoms in these regions) and could significantly impact the air quality, i.e. tropospheric ozone and SOA formation.

74. UPTAKE OF PEROXY RADICALS ON ORGANIC AEROSOLS: DEVELOPMENT OF AN AEROSOL FLOW TUBE AND MOLECULAR-LEVEL CHARACTERIZATION

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Abstract

Many uncertainties are still associated to chemical reaction mechanisms used in atmospheric models, in particular for RO_x radicals (OH, HO₂, RO₂). Recent measurements of radicals in forested areas characterized by low NO_x (NO₂, NO) concentrations indicate that models can significantly overestimate peroxy radical concentrations (Griffith et al., *Atmos. Chem. Phys.* 13, 5403 (2013); Mao et al., *Atmos. Chem. Phys.* 12, 8009 (2012)). These results question the models' capability to describe correctly the oxidative capacity of the troposphere since peroxy radicals are a main source of OH, one of the most important oxidative species in the atmosphere (D. Stone et al., *Chem. Soc. Rev.* 41, 6348 (2012)). One possible explanation is the occurrence of heterogeneous processes (uptake of radicals) on the surface of aerosols that are not included in models. While recent studies have reported uptake coefficients of HO₂ on aerosols, uptakes of RO₂ radicals have yet to be investigated.

The aim of this work is to investigate the HO₂ and RO₂ uptakes on organic aerosol surfaces, both theoretically and experimentally. An experimental setup (Aerosol Flow Tube, AFT) using a PERCA (PEroxy Radical Chemical Amplification) system to measure HO₂ and RO₂ has been built and the first validation steps (Aerosol and radicals wall losses, reaction time, etc) will be described. Two Aerosol generation systems have also been built and characterized. Complementary to the experiments, a molecular modeling study is also carried out using quantum mechanics (QM) and molecular dynamics (MD) methods.

This work was supported by the CaPPA project (Chemical and Physical Properties of the Atmosphere), funded by the French National Research Agency (ANR) through the PIA (Programme d'investissement d'avenir) and by the regional council "Hauts-de-France". The authors also thank CPER Climibio and FEDER for their financial support. Calculations were performed using HPC resources from GENCI-TGCC (Grant 2017-A0010806820). The "Centre de Ressources Informatiques" (CRI) of the Université de Lille also provided computing time.

75. PHOTOCHEMICAL DEGRADATION AND PRODUCTION OF POLYCYCLIC AROMATIC HYDROCARBONS AND CARBOXYLIC ACIDS IN CANADIAN HIGH ARCTIC AEROSOLS (ALERT) BEFORE AND AFTER POLAR SUNRISE

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Abstract

The Arctic is surrounded by the North American and Eurasian continents, which is recognized to receive polluted air masses containing organic and inorganic contaminants from the northern midlatitudes by long-range atmospheric transport (P. Fu et al., ES&T, 43, 286–292, 2009; LA. Barrie. AE, 20, 643–663, 1986).. In this study 19 polycyclic aromatic hydrocarbons (PAHs) containing minor sulfur containing heterocyclic PAH (dibenzothiophene) and major 6 carcinogenic PAHs were identified with an elevated proportion of fluoranthene followed by benzo[k]fluoranthene, pyrene, and chrysene. However, their concentrations significantly dropped owing to photochemical decomposition in the sunlit period of spring. During the polar sunrise from mid-March to mid-April, benzo[a]pyrene to benzo[e]pyrene ratios significantly declined, and the ratios diminished further from late April to May onward. Results suggest that PAHs transported over the Arctic are subjected to strong photochemical degradation at polar sunrise. Concentrations of some aromatic acids such as benzoic and phthalic acids increased in the course of polar sunrise, signifying that aromatic hydrocarbons are oxidized to result in aromatic acids. However, PAHs do not act as the major source for low molecular weight (LMW) diacids such as oxalic and malonic acids, which are largely produced at polar sunrise in the arctic atmosphere, as PAHs are 1 to 2 orders of magnitude less abundant than LMW diacids. Higher concentrations of PAHs and aromatic acids in the Alert aerosols before polar sunrise specify hints to better understand the role of photochemical processes in the mid latitudes and long-distance transport to the Arctic. Lower concentrations of PAHs and aromatic acids after polar sunrise imply a photochemical degradation of combustion-derived PAHs and secondary production of organic aerosols in the presence of oxidants in the Arctic atmosphere. Long-range atmospheric transport of aerosols and their precursor gases are the main sources of the arctic winter aerosols. Another aspect of this study can also be the gas kinetics which would be performed as a follow up research.

76. HYDROXYL RADICAL INITIATED PHOTO-OXIDIZATION OF SERIES OF BUTADIENES IN TROPOSPHERE: AN EXPERIMENTAL AND COMPUTATIONAL STUDY

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Abstract

The photo-oxidation of butadienes play a significant role in the formation of Secondary Organic Aerosols (SOAs) under NO_x (nitrogen oxides) rich environments.[1] These compounds significantly contribute to the formation of ozone in the troposphere because of proliferation and high chemical reactivity in the generation of peroxy radicals.[2] The hydroxyl radical initiated oxidation of butadienes establishes the balance of hydrogen oxides (HO_x = OH + HO₂).[3] These compounds are being released into the atmosphere due to incomplete combustion of auto mobile exhausts, gasoline, diesel fuels, petroleum refining, rubber industries, plastic and subsequent industries etc.[3] The kinetic data and mechanistic study of individual compounds are essential to predict the possible contribution of these compounds to the atmospheric adverse effects such as air pollution and climate change.

Temperature dependent rate coefficients were measured for the reaction of 2,3-dimethyl-1,3-butadiene with hydroxyl radical over the temperature range of 263-363K using relative rate experimental techniques. Measured rate coefficients were used to fit the Arrhenius equation and is $k_{2,3\text{-dimethyl-1,3-butadiene+OH}}(269\text{-}363\text{K}) = (1.92 \pm 0.46) \times 10^{-11} \exp[(490 \pm 76)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. To understand the reaction mechanism and to complement our experimental results, extensive computational calculations were performed over the temperature range of 200-400K for reaction of OH radical with 2,3-dimethyl-1,3-butadiene using Canonical Variational Transition state theory (CVT) with Small Curvature Tunnelling (SCT) in combination with QCISD(T), CCSD(T), MP2 level of theories. To understand the atmospheric implications of butadienes, the obtained rate coefficients were compared with 1,3-butadiene and 2-methyl-1,3-butadiene (isoprene). Atmospheric lifetimes, global warming potentials and ozone formation potentials of these butadienes will be discussed in detailed in the conference.

77. ELEVATED LEVELS OF OH OBSERVED IN HAZE EVENTS DURING WINTERTIME IN BEIJING, AND THE COMPARISON OF RADICAL MEASUREMENTS WITH BOTH STEADY STATE CALCULATIONS AND BOX MODEL SIMULATIONS.

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Abstract

We will present OH, HO₂ and RO₂ measurements made in central Beijing during the recent 'An Integrated Study of AIR Pollution PROCesses in Beijing (AIRPRO)' project which took place in November/December 2016 and May/June in 2017. Interference free OH measurements were made using the FAGE (Fluorescence Assay by Gas Expansion) technique, with the use of an inlet pre injector (IPI) which provides an alternative method to determine the background by injecting a scavenger (propane) to remove ambient OH. The chemical conditions varied enormously between the two campaigns, with NO concentrations exceeding 250 ppb in the winter, whilst O₃ levels over 100 ppbv were frequently observed during the summer. The average OH concentration during the winter campaign was surprisingly high ($\sim 2.5 \times 10^6 \text{ cm}^{-3}$) even during haze events, and during the summer elevated levels of OH were observed, the highest we have ever measured reaching up to $2.5 \times 10^7 \text{ cm}^{-3}$.

A comparison of OH observations with a steady state calculation, constrained to the total OH reactivity measurement and known OH precursors that were measured alongside OH, has been performed. The steady state calculation was able to reproduce the OH observations well during the winter, but highlighted a significant missing daytime source of OH under low NO conditions during summer. A comparison between the observed radicals and a box model constrained with co-located measurements and using the detailed Master Chemical Mechanism demonstrates that wintertime OH concentrations can be reproduced under low-NO_x conditions, but are underestimated at NO concentrations beyond 4 ppbv. This underestimation of OH under high NO_x correlates with an underestimation of HO₂ and RO₂ and highlights uncertainties in our understanding of the reactions and transformations of peroxy radicals in high NO conditions. The summer measurement-model comparisons also highlighted similar discrepancies during periods when NO was high. In agreement with the steady state calculation, the model-measurement comparison provides evidence of a missing source of OH under low-NO_x conditions in the presence of high loadings of VOCs, which is similar to other studies in China under low NO and also in rainforests.

78. OH INITIATED STUDY OF THE OXIDATION OF N,N'-DIMETHYLFORMAMIDE: EVIDENCE FOR QOOH+O₂ FORMING OH

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Abstract

A FAGE sampled high pressure reactor (Stone et al., RSI, 87, pp-054102 (2016)) has been used to investigate the kinetics of OH initiated chemistry of dimethyl formamide ((CH₃)₂NC(O)H, DMF). The reactor can study kinetics over high pressures (tested to >3 bar, N₂/O₂, potentially able to run to 10 bar) and temperatures (295 – 800 K), where the reaction is initiated (Stone et al., 2016) by flash photolysis (248 nm, 266 nm) of hydrogen peroxide.

The reaction is monitored by following the OH radical sampled from the reactor via a pinhole, and then detecting the OH in the jet-expanded gas, using off-resonance laser induced fluorescence at 282 nm. The reactor is also sampled by a PTR-TOF-MS which provides end product analysis, including imine formation from amides.

Between 295 – 470 K, single exponential kinetics were observed for the OH and DMF reaction, and the kinetic parameters derived were in good agreement with the literature values of Solignac et al. (2005) and Bunkan et al. (PCCP, 17, pp7046-7059 (2015)). However, at T > 470 K, in the presence of O₂, the OH kinetics were non-single exponential, indicating that OH is recycled. The recycling kinetics were determined over the temperature range 470-650 K, and a range of added O₂: 1.5 × 10¹⁶- 3 × 10¹⁸ molecule cm⁻³.

The source of this OH recycling has been investigated by performing reaction rate theory calculations on the theoretical potential energy surfaces (PES) — of Bunkan et al. (2015) and our own ab initio calculations — using the master equation program MESMER. Experimentally, there was no evidence of well-skipping OH recycling at low pressures (P < 10 Torr). The lack of well skipping OH, coupled with the MESMER analysis, shows that the R+O₂ → RO₂ → QOOH → OH surface is not the source of the observed OH recycling.

The MESMER analysis showed an oxygen dependent competition between aldehydic R radical decomposition and OOQOOH formation, which was experimentally observed; this is indicative of a competition between pathways where interception by oxygen is in competition with a direct R decomposition channel. It is noted that, unusually for such systems, QOOH is lower in energy than RO₂, therefore, in this system it is efficient to intercept QOOH with O₂ to form O₂QOOH. O₂QOOH are a known source of OH and so it is reasonable to infer that this was a source of the OH observed.

80. UNIMOLECULAR DECOMPOSITION KINETICS OF THE STABILISED CRIEGEE INTERMEDIATES CH₂OO AND CD₂OO

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Abstract

Recent interest in Criegee intermediates, produced in the atmosphere following the ozonolysis of unsaturated volatile organic compounds (VOCs), has largely focused on the chemistry of their bimolecular reactions. However, the unimolecular decomposition reactions of stabilised Criegee intermediates are potentially significant as loss mechanisms in the atmosphere.

In this work, we report the results of an investigation of the unimolecular decomposition kinetics of the stabilised Criegee intermediates CH₂OO and CD₂OO, produced following the flash photolysis of CH₂I₂ and CD₂I₂, respectively, in the presence of excess O₂.

Experiments have been performed as a function of temperature and pressure, with direct monitoring of the Criegee intermediate by time-resolved cavity-enhanced broadband UV absorption spectroscopy. Laser-induced fluorescence (LIF) spectroscopy experiments were also conducted over a range of temperatures and pressures to monitor the production of OH radicals following the decomposition of CH₂OO.

Experimental results have been used to constrain Master Equation calculations using the Master Equation Solver for Multi Energy-well Reactions (MESMER) to model the decomposition reaction and to enable a full description of the decomposition kinetics as a function of temperature and pressure. The results indicate that the decomposition of CH₂OO leads to production of H₂ + CO₂ (63.7 % yield), H₂O + CO (36.0 % yield), and OH + HCO (0.3 % yield). A parameterisation of the decomposition kinetics for use in atmospheric models is provided, and implications of the results will be discussed.

81. UNRAVELLING THE REACTION MECHANISMS OF IODOUS ACID WITH CHLORINE ATOM

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Abstract

Because of their possible implications in the destruction of the stratospheric ozone layer, chlorine oxides have drawn the attention of atmospheric chemists. For instance the reaction of HOIO, HOOI with Cl led to the formation of HCl, HOCl, ClO, HOI, IO and OIO species. Despite the importance of iodous acid (HOIO) in atmospheric and nuclear chemistry, computational studies on HOIO species are scarce. The main objective of this work is to provide reliable kinetic and thermodynamic data for the gas phase reaction of iodous acid isomers (HOIO and HOOI) with chlorine atoms. Several reaction pathways are studied in order to assess their branching ratios: H-abstraction, I-abstraction, OH-abstraction, IO-abstraction. The reaction mechanism involves many stationary points on the potential energy surface and reveals some unusual features for the H-abstraction. The theoretical calculations were performed with the augmented correlation consistent basis sets aug-cc-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. Then, the single-point energies at the DFT structures were calculated using coupled cluster theory (CCSD(T)) and the weighted core-valence basis sets aug-cc-pwCVnZ (n = D, T, Q). Core-valence calculations were carried out at the CCSD(T)/aug-cc-pwCVTZ level of theory. The scalar relativistic corrections were computed at the CISD/aug-cc-pVTZ level of theory.

Acknowledgments: We appreciate the support from the French ANR agency under Contract No. ANR-11-LAB-0005 "Chemical and Physical Properties of the Atmosphere" (CaPPA), "ANR-11-RSNR-0013-01" (MiRE). Computer time for part of the theoretical calculations was kindly provided by CRI Lille and CRIANN. We thank the Slovak Research and Development Agency (Project APVV-15-0105) for support

82. PRODUCTS AND MECHANISMS OF THE REACTIONS OF A SERIES OF HYDROFLUOROALKENES INITIATED BY OH RADICALS

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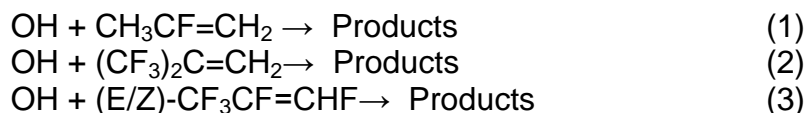
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Abstract

Fluorinated compounds are environmentally persistent and have been demonstrated to bioaccumulate and contribute to climate change¹. As a result, alternatives are being proposed fluorinated compounds that have lower atmospheric lifetimes and Global Warming Potential (GWP), which include the hydrofluorinated alkenes². Within hydrofluoroalkenes (HFAs), 2-fluoropropene (2-FP), (E/Z)-isomeric mixture of 1,2,3,3,3-pentafluoropropene (PFP) and 3,3,3-trifluoro-2-(trifluoromethyl) propene (HXFP) are widely use in industrial applications as alternatives refrigerants; in pharmaceutical uses and production of perfluorinated polymers³. In this work we have studied the atmospheric degradation pathways of the reaction of HFAs with OH radicals:



The following reaction products have been identified and quantified:

CH₃C(O)F, HC(O)H (1), CF₃C(O)CF₃, HC(O)H (2) and CF₃C(O)F, FC(O)H (3).

The experiments were performed at 1000 mbar of synthetic air using an atmospheric simulation chamber of 480 L capacity. The products mentioned above are the majority products of these reactions. The result indicates that the products proceed of the alcoxy intermediated of the reactions of OH radicals with HFAs by initial addition of OH to the >C=C< bond.

The results will contribute to an improved representation of the degradation of fluorinated alkenes in the atmospheric chemical models used to assess the environmental impact of chemicals and their contribution to the oxidizing capacity of the atmosphere.

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83. EPOXIDE FORMATION IN THE DECOMPOSITION OF MBO232

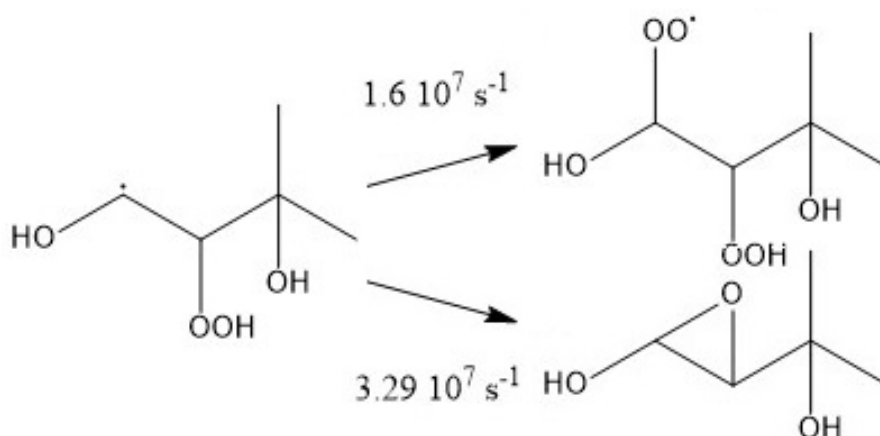
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Abstract

The oxidation of volatile organic compounds (VOC) is investigated to gather a better understanding of the oxidative properties in the atmosphere. The decomposition of 2-methyl-3-butadiene-2-ol (MBO232) was theoretically investigated by (H. Knap et al, Atmospheric Environment, 147, pp. 79-87, 2016) but did not explain the discovered epoxide tracers found in (H. Zhang et al, Environ. Sci. Technol., 46, 9437–9446, 2012) in chamber experiments. In this study, a formed alkyl radical in (H. Knap et al, Atmospheric Environment, 147, pp. 79-87, 2016) is used, to form an epoxide by reacting with the first oxygen in a neighboring substituted peroxide group. The reaction is calculated with Transition State Theory (TST) using energy barriers including zero point vibrational energies calculated at wB97XD/aug-cc-pVTZ level of theory. The conformers of the reactant, transition state and product with the lowest zero point corrected energy are used to calculate the energy barrier. The calculated rate constant is $3.29 \times 10^7 \text{ s}^{-1}$, which means the formation of epoxide competes with the O₂ addition to the alkyl radical with a rate constant of approximately $1.6 \times 10^7 \text{ s}^{-1}$. This concludes that not all alkyl radicals will react with molecular oxygen, but will lead to formation of epoxides.



84. RATE COEFFICIENTS FOR THE GAS PHASE REACTIONS OF CHLORINE ATOMS WITH A SERIES OF EPOXY COMPOUNDS

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Abstract

Epoxy compounds are used on the large scale in industry as solvents and feedstock in the manufacturing of chemicals. Additionally, there is huge interest on developing their applications as possible additives and alternative fossil fuels compounds. To date only limited information on the gas phase reactivity of this class of compounds exists.

In this work we present the first kinetic investigation of the reaction of chlorine atoms with cyclohexene oxide (CHO), 1,2-epoxyhexane (EHX), 1,2- epoxybutane (12EB), trans-2,3-epoxybutane (tEB) and cis-2,3-epoxybutane (cEB). Experiments have been performed in a 1080 l Quartz reactor (QUAREC) and a 480 l Duran glass chamber at Wuppertal University, Germany. The rate coefficients were determined using the relative rate method. The following room temperature reaction rate constants were obtained (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$): $k_{\text{CHO}} = (2.40 \pm 0.87) \times 10^{-10}$, $k_{\text{EHX}} = (1.77 \pm 0.63) \times 10^{-10}$, $k_{12\text{EB}} = (8.43 \pm 2.55) \times 10^{-11}$, $k_{\text{tEB}} = (6.99 \pm 2.09) \times 10^{-11}$ and $k_{\text{cEB}} = (6.92 \pm 2.15) \times 10^{-11}$. The errors quoted for the rate coefficients include the 2σ statistical error from the linear regression analyses of the experiments and up to 35% contribution in the recommended values of the rate coefficients for reference compounds with chlorine.

This is to our knowledge the first kinetic study of the reaction of these compounds with Cl atoms. Atmospheric lifetimes, reactivity trends and atmospheric implications will be discussed considering the epoxy compound rate coefficients obtained in the present study.

These results from our study will help to elucidate the gas phase chemical degradation mechanisms of this class of compounds and to explore their environmental impact with respect to ozone and secondary organic aerosol formation.

85. REACTIVITY OF HYDROFLUOROPOLYETHERS TOWARDS OH: A COST-EFFECTIVE IMPLEMENTATION OF MC-TST

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Abstract

Adverse environmental impact of CFC release into the atmosphere [1,2] has led to an international effort to replace them with acceptable alternatives. The Montreal Protocol phased out CFCs in industrialized countries because of their elevated ozone depletion and global warming potentials (ODP and GWP). Development of environmentally friendly replacements with lower tropospheric lifetimes became urgent, with HCFCs, HFCs and PFCs selected as first- and second-generation replacements. However, non-zero ODP and high GWP were still an issue, with HFCs and PFCs targeted by the Kyoto Protocol because of their high GWP. The design and development of useful alternatives continued, with hydrofluoropolyethers (HFPEs) appearing as promising third-generation replacements (zero ODP and even lower GWP).

Here, we will provide a detailed insight behind the computational strategies used in predicting the reactivity of different HFPEs towards the OH radical. Having a general formula of $R-(OCF_2CF_2)_p(OCF_2)_q-OR$ ($R=CF_2H, CH_3, CH_2CH_3, CH_2CH_2CH_3, CH(CH_3)_2$), we have calculated nine rate constants: all five possible cases for $p \geq 1, q = 1$, $p \geq 1, q = 0$ ($R=CF_2H, CH_3$), $p = 0, q \geq 2$ ($R=CH_3$) and $p = 2, q = 0$ ($R=CH_3$). In the absence of any reported theoretical results, the quality of our cost-effective approach [3] (with M08-HX/aug-cc-pvtz-2//M08-HX/pcseg-1 DFT calculations and using Eckart tunneling) based on multiconformer transition state theory (MC-TST) [4] will be assessed by comparison with four experimental rate constants [5,6]. Our investigations yield rate constants averaging a factor of ~ 0.7 (k_{MC-TST}/k_{exp}) of experimental data.

The good agreement with experimental results provides a valid framework for present and future calculations, where this cost-effective approach will prove essential in understanding the atmospheric chemistry of HFPEs. Additionally, we hope to use this methodology as an important tool in the development of new greener CFC alternatives.

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86. VIBRATIONALLY EXCITED PRODUCTS OF ROAMING REACTIONS IN THE ATMOSPHERE AS A NOVEL SOURCE OF HYDROXYL RADICALS

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Abstract

Hydroxyl (OH) and hydroperoxyl (HO₂) are the most important radicals in the atmosphere. Reaction with OH is the leading mechanism for the removal of most volatile organic compounds (VOCs) from the atmosphere. Deficiencies in the concentrations of these radicals calculated by atmospheric models has led to unknown reactions of carbonyls being suggested as the missing source of these radicals. Roaming photodissociation mechanisms such as those exhibited by formaldehyde (H₂CO) and acetaldehyde (CH₃CHO) are proposed as these unknown reactions. H₂ and CH₄ fragments formed from these roaming mechanisms are born exceptionally hot, with enough internal energy to overcome the usually prohibitive 230 kJ/mol barrier to reactions with atmospheric O₂, potentially forming hydroxyl and hydroperoxyl radicals. Using velocity map imaging (VMI) and continuous wave cavity ring down spectroscopy (cw-CRDS) techniques, the potential reaction schemes of these hot fragments are being investigated, with a particular focus on reaction energetics and rates. If this research is successful, roaming reactions may be able to account for the incongruous levels of OH and HO₂ in the atmosphere, and vastly improve our understanding of the dynamics of these radicals in these environments.

87. STUDY OF KEY OH + NO_x/NO_z REACTIONS UNDER UPPER TROPOSPHERE / LOWER STRATOSPHERE CONDITIONS

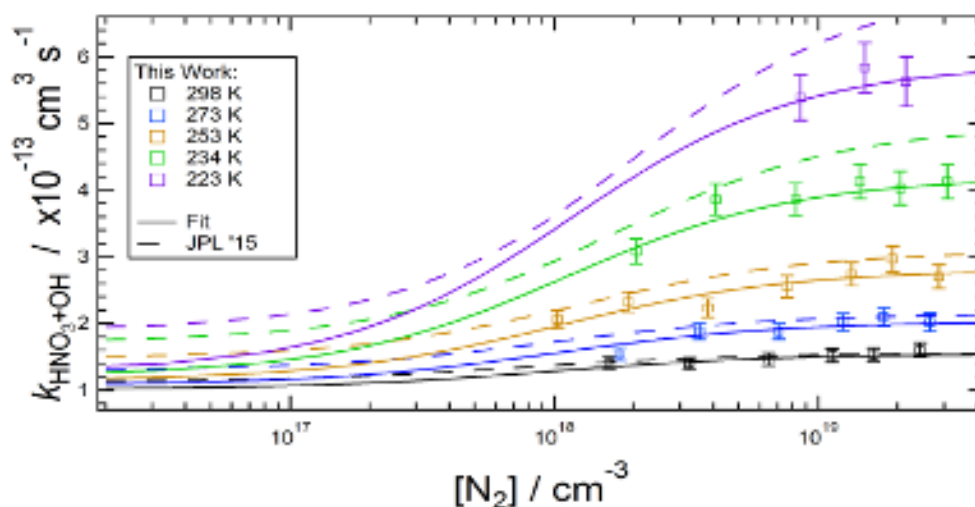
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Abstract

The oxidation of NO_x (NO + NO₂) and NO_z (e.g. HONO₂) species play an important role in the upper troposphere/lower stratosphere (UT/LS). The OH initiated oxidation of NO₂ and HONO₂ play important roles in controlling the O₃ budget, removing HO_x radicals whilst NO_x budgets in the UT/LS. A recent modelling study has highlighted the significance of these reactions in affecting the ozone radiative forcing potential, rating them as the 1st and 9th most important reactions based on the current uncertainty estimation quoted in the JPL Kinetic Data Evaluation. Currently, the recommended uncertainty in $k_{\text{OH}+\text{NO}_2}$ is 30% ($\pm 1\sigma$) and $k_{\text{OH}+\text{HONO}_2}$ is 20% ($\pm 1\sigma$) at STP, but under UT/LS conditions (low T and p), the uncertainty could increase to as much as $\pm 50\%$, which would have a significant impact on atmospheric models. We will present experimental results into the OH + NO₂ and HONO₂ rate coefficient over the matrix of temperature (220 – 300 K) and pressure (25 – 750 Torr) using OH (A ← X) Laser Induced Fluorescence (LIF). Specifically, our results represent the determination of $k_{\text{OH}+\text{HONO}_2}(T,p)$ using two different and complementary in-situ [HONO₂] measurements over an extended pressure range, and the first determination of $k_{\text{OH}+\text{NO}_2}(T,p)$ using in-situ detection of [NO₂]. Experimental results will be discussed along with MESMER calculations and atmospheric impact modelled using the STOCHEM-CRI global model.



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88. MICROCANONICAL INSTANTON RATE THEORY APPLIED TO MOLECULAR REACTIONS

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Abstract

Instantons describe the tunneling pathways that dominate quantum dynamics at low temperatures. Moreover, they provide a link between the classical and quantum mechanical descriptions of chemical kinetics in what is called semiclassical transition state theory (SCTST) [1]. Derived from Feynman's path integral method, this theory allows for efficient computation of reaction rates in systems where the full quantum description would be too demanding [2]. So far SCTST has almost exclusively been used to calculate thermal rate constants $k(T)$ and it has had great success in reproducing experimental rates below the crossover temperature.

Here, however, we present a new microcanonical instanton formulation of SCTST which allows us to calculate accurate energy-dependent rates $k(E)$ [3]. Our rigorous method is able to include quantum effects such as tunneling and zero point energy while keeping the resourcefulness of a classical rate calculation. This theory will be very useful to kineticists, especially in the fields of astro- and atmospheric chemistry, who would like energy resolved rates for molecular reactions over all energy ranges.

In order to verify the quality of microcanonical SCTST, tests were run on various adiabatic potential energy surfaces where quantum effects have a large effect on the reaction rate and where scattering results are available for direct comparison. Our results are able to reproduce the scattering rates remarkably well and with very little computational resources. Future work will focus on finding a more accurate way to calculate the zero-point energy for molecular systems and to apply this theory to larger systems in atmospheric chemistry.

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89. KINETICS OF THE ATMOSPHERICALLY RELEVANT GAS-PHASE REACTIONS OF ALLYL CYANIDE

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Abstract

Allyl cyanide was found in 1863 in mustard oil and since then, it has also been detected in cruciferous vegetables such as cabbage, broccoli, cauliflower and sprouts, being its production higher when the leaves of these vegetables are damaged. (L. G. West et al., *JAF*, 25, pp. 1234-1238 (1997); H. Tani et al., *FCT*, 42, pp. 453-458 (2004)) Moreover, allyl cyanide is one of the nitriles widely used in the manufacture of plastics, solvents, and synthetic intermediates. In fact, thermal degradation of acrylonitrile-based plastics leads to the emissions of a large variety of nitriles, including allyl cyanide. (M. M. Shapi et al., *JCB*, 562, pp. 681-696 (1991)) Therefore, allyl cyanide may be released into the atmosphere from both biogenic and anthropogenic sources and it is important to know its reactivity towards the different tropospheric oxidants.

The aim of this work is to determine the rate coefficients and reaction products of the gas-phase reactions of ally cyanide with tropospheric oxidants, such as chlorine (Cl) atoms, hydroxyl (OH) radicals, and ozone (O₃). An atmospheric simulation chamber has been used for the study of the proposed reaction at 298 ± 2 K and 760 ± 5 Torr under free-NO_x conditions. A relative kinetic method has been employed in which Fourier transform infrared spectroscopy (FTIR) has been used as quantification technique of allyl cyanide and the reference compound (cyclohexane or ethanol). (A. A. Ceacero-Vega et al., *JPCA*, 116, pp. 4097-4107 (2012)) FTIR and gas chromatography-mass spectrometry coupled to solid phase micro-extraction (GC-MS/SPME) have been used to detect and quantify, when possible, the reaction products.

90. AN INTER-COMPARISON OF FAGE AND CRDS FOR THE DETECTION OF HO₂ AND CH₃O₂ RADICALS IN A SIMULATION CHAMBER

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Abstract

HO₂ is an important species in the atmosphere, as it is involved in the HO_x radical reaction cycle that is critical to the oxidation of atmospheric pollutants and the ultimate cleaning of the troposphere. One of the most widely utilised methods to measure HO₂ is Fluorescence Assay by Gas Expansion (FAGE), which indirectly measures HO₂ by sampling into a low pressure cell and titrating HO₂ with NO to produce OH that is then detected by Laser Induced Fluorescence. This is an indirect and non-absolute detection technique that requires calibration to convert the measured signal into [HO₂], typically involving the photolysis of H₂O at 185 nm to produce OH and HO₂. This calibration is subject to ~30 % errors at 2σ level. Another key component of the HO_x cycle is the CH₃O₂ radical, which is currently not routinely measured in the atmosphere. We have developed a sensitive and speciated detector for CH₃O₂ radicals that is based upon this same FAGE technique as HO₂ detection (L. Onel et. al., AMT, 10, pp. 3985-4000 (2017))

The work presented here shows the validation of the FAGE technique and its calibration procedure for both HO₂ and CH₃O₂ radicals through inter-comparison experiments between the non-absolute FAGE technique and Cavity Ringdown Spectroscopy (CRDS), an absolute absorption based method. The CRDS system features a cavity length of ~1.2 m and a total path of ~60 km, and was detect HO₂ and CH₃O₂ at 1506 nm and 1335 nm. The experiments were performed inside the 2.25 m³ stainless steel Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC), using a synthetic air mixture at 150 and 1000 mbar of pressure and 298 K. Radicals were generated by photolysis of Cl₂ at 365 nm in the presence of O₂ and CH₃OH or CH₄ for HO₂ and CH₃O₂ respectively, and the radical concentration was monitored using both instruments simultaneously.

A good agreement between the two detection methods was found, with FAGE measurements falling within 11% and 14% of the CRDS measurements for HO₂ (L. Onel. et. al., AMT, 10, pp. 4877-4894 (2017)) and CH₃O₂ respectively. This consistency reinforces the FAGE calibration method for HO₂, which is widely used for field measurements in the atmosphere, and it validates the newly developed method for CH₃O₂.

91. ATMOSPHERIC DEGRADATION OF (E)-4-METHOXY-3-BUTEN-2-ONE AND 1-(E)-1-METHOXY-2-METHYL-1-PENTEN-3-ONE INITIATED BY OH RADICALS: KINETICS AND REACTION PRODUCTS.

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Abstract

Ketones are one of the dominant groups of oxygenated hydrocarbons found in the lower troposphere. These can be emitted into the atmosphere by anthropogenic activities, such as industrial processes and personal uses but also from gasoline and diesel-fuelled vehicles. Furthermore, ketones are also formed extensively as reaction products of other volatile organic compounds in the troposphere.¹⁻³

In the present study the kinetics of the gas-phase reactions of hydroxyl radicals with two unsaturated methoxy-ketones at (298 ± 3) K and 1 atm have been studied for the first time using the relative rate technique in an environmental chamber with in situ FTIR detection of reactants. The rate coefficients obtained using propene and isobutene as reference compounds were (in units of $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) as follows: $k_1(\text{OH} + (\text{E})\text{-4-methoxy-3-buten-2-one}) = (1.42 \pm 0.66)$, and $k_2(\text{OH} + 1\text{-(E)-1-methoxy-2-methyl-1-penten-3-one}) = (3.34 \pm 0.58)$.

In addition, identification of the main degradation products and the degradation pathways for these reactions were performed. The reaction products found, together with the observed reactivity trends, confirm that the reactions proceed via an addition mechanism of the OH radical to the double bond.

The atmospheric lifetimes toward the major tropospheric oxidants have been estimated and possible atmospheric implications assessed.

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92. GAS-PHASE OXIDATION OF AROMATIC HYDROCARBONS: A KINETIC STUDY OF THE OH REACTION WITH METHOXYBENZENES AT ATMOSPHERIC CONDITIONS

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Abstract

Methoxybenzenes are widely used in industrial activities, such as pharmaceuticals¹, cosmetics² and agricultural pest control (formulating insect attractants)^{3,4}. They were also identified among the oxygenated aromatic compounds emitted during biomass burning in both the gas and aerosol phases.⁵⁻⁷ Furthermore, trimethoxybenzene based compounds are potentially toxic in nature and cause numerous health problems. They are found in many hazardous waste dumps, which have been included in the national priority list proposed by the U.S. environmental protection agency.⁸

Rate coefficients for methoxybenzene, 1,2,3-trimethoxybenzene, 1,2,4-trimethoxybenzene and 1,3,5-trimethoxybenzene reacting with hydroxyl radicals have been studied in a 1080 L simulation chamber at atmospheric conditions using the relative kinetic method. The following rate coefficients ($\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$) were determined: $(2.86 \pm 0.12) \times 10^{-11}$ for methoxybenzene, $(7.70 \pm 0.36) \times 10^{-11}$ for 1,2,3-trimethoxybenzene, $(1.29 \pm 0.56) \times 10^{-10}$ for 1,2,4-trimethoxybenzene and $(1.56 \pm 0.69) \times 10^{-10}$ for 1,3,5-trimethoxybenzene. By comparing methoxybenzenes with a different number of $-\text{OCH}_3$ groups it was observed that depending on the number of the substituents at the aromatic ring, the rate constant with OH radicals could be organized as follows: $k_{\text{Trimethoxybenzenes}} \gg k_{\text{Dimethoxybenzenes}} > k_{\text{methoxybenzene}}$. Calculated atmospheric lifetimes, in the range of a few hours indicate that methoxybenzenes are likely to be removed rapidly in the gas-phase by reaction with OH radicals.

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93. RATE CONSTANTS FOR THE REACTION OF OH RADICALS WITH HYDROCARBONS IN A SMOG CHAMBER AT LOWER ATMOSPHERIC TEMPERATURES

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Abstract

The reaction of OH radicals with the hydrocarbons n-butane, n-pentane, n-hexane, n-heptane, n-octane, n-nonane, cyclooctane, 2,2-dimethylbutane, 2,2-dimethylpentane, 2,2-dimethylhexane, 2,2,4-trimethylpentane, 2,2,3,3-tetramethylbutane, benzene, toluene, ethylbenzene, o-xylene and p-xylene was investigated at 288 and 248 K in a temperature controlled smog chamber. OH radicals were produced by photochemical degradation of methyl nitrite. All 17 hydrocarbons and n-perfluorohexane (PFH) were present simultaneously at the ppb level and monitored by gas chromatography, and rate constants were determined from relative rate calculations with a selected number of reference compounds. The results from this work at 288 K (three chamber runs) show good agreement with previous literature data, indicating a convenient method to study the reaction of OH radicals with many hydrocarbons simultaneously. Moreover, we extend the useful range of data to 248 K (two runs; preliminary values of k in units of $10^{-12} \text{ cm}^3\text{s}^{-1}$ relative to n-pentane = 2.93 alone) for 2,2-dimethylpentane (2.96 ± 0.02), 2,2-dimethylhexane (4.28 ± 0.03), 2,2,4-trimethylpentane (3.19 ± 0.03) and ethylbenzene (7.41 ± 0.18) and o-xylene (16.3 ± 1.0), where the information on the temperature dependence for o-xylene and ethylbenzene has become available for the first time. Evaluation methods and their limitations will be discussed.

Results from this work are useful to determine the lifetime of the hydrocarbons over the tropospheric temperature range and are essential for modeling the photochemical reactions of hydrocarbons in the real troposphere.

94. GAS PHASE KINETIC STUDY OF THE OH RADICAL INITIATED OXIDATION OF ALKYL FURANS AT ATMOSPHERIC PRESSURE AND 298±2 K

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Abstract

Furans are emitted in the atmosphere from anthropogenic activities and biogenic sources. They are potential source of ozone generation and secondary organic aerosol formation due to its high atmospheric reactivity against the main atmospheric oxidants (Calvert et al., 2011).

Rate coefficients for the gas-phase OH radical initiated oxidation of furan (FN), 2-methylfuran (2-MF), 2,3-dimethylfuran (2,3-DMF), 2,5-dimethylfuran (2,5-DMF), 2,3,5-trimethylfuran (TrMF) and tetramethylfuran (TeMF) have been investigated using relative kinetic technique. The experiments were performed in the ESC-Q-UAIC quartz glass photoreactor at a total air pressure of 1000±5 mbar and temperature of 298±2 K using Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatography (GC) techniques for reactants monitoring. Photolysis of methyl nitrite at 365 nm has been used for OH radical generation. The following reference compounds have been employed in these investigations: acrolein, mesitylene, *E*-2-butene, propene and furan.

For the investigated (alkylated)-furans significant agreement was observed between rate coefficient values obtained with different reference compounds. Analysis of the experimental data proved that (alkylated)-furans series reactivity toward OH radical is increasing with the number of methyl groups added on the ring. In the investigated furan series rate coefficient values increased from furan ($k_{FN} = (3.16 \pm 0.12) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) with about one order of magnitude to higher (alkylated)-furans.

The results are discussed in comparison with available literature data and SAR estimated values. These kinetic studies represent first reported rate coefficient values for reaction of TrMF and TeMF with OH radical. The kinetic results will be presented together with an assessment of the atmospheric importance of furans OH radical initiated degradation.

Acknowledgements:

The financial support provided by UEFISCDI within the PN-III-P4-ID-PCE-2016-0807 (IGAC-CYCLO) and PN-III-P2-2.1-PED-2016-1621 (CHARUSO) 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.

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95. TEMPERATURE DEPENDENCE KINETIC STUDIES BY USING THE NEWLY THERMOSTATED ESC-Q-UAIC CHAMBER

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Abstract

Studying temperature dependence for the gas-phase rate coefficients of atmospheric pollutants with relevant oxidative species is of utmost importance for understanding atmospheric processes. ESC-Q-UAIC (Environmental Simulation Chamber made of Quartz from the "Alexandru Ioan Cuza", University of Iasi) facility has been updated with a temperature regulation system that allows studies to be performed at various temperatures from 0°C to 40°C. Reaction in the gas-phase of dimethyl sulfide (DMS) with OH radicals has been investigated in the ESC-Q-UAIC facility for validation purposes of the newly developed temperature regulation system. Kinetic experiments were performed in synthetic air at a total pressure of 1000 mbar and four different temperatures (275, 283, 293 and 303 K). The temperature regulation system was able to keep the temperature over the experimental period within ± 1 degree. Cyclohexane and propene were used as reference compounds. Photolysis of H₂O₂ at 254 nm was used as the OH radical source. The concentration–time behavior of DMS and the reference organic compounds was followed over 30 min time periods by FTIR long path spectroscopy. Data evaluation allowed inferring the following Arrhenius expression from the performed measurements: $k = (2.00 \pm 0.06) \times 10^{-13} \exp [(1108 \pm 126.6)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ with a negative Arrhenius activation energy of $(-9.21 \pm 1.05) \text{ kJ/mol}$. The data are in good agreement with other reports^{1,2}. Results obtained from the present study allowed us to validate the newly temperature regulation system integrated into the ESC-Q-UAIC facility. Appropriate operation for at least four different temperatures, such as those used in the present study, is encouraging in using the thermostated ESC-Q-UAIC chamber for performing other gas-phase experiments that involve temperature as an important experimental parameter.

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Acknowledgements:

The authors acknowledge the financial support provided by UEFISCDI within the PN-III-P2-2.1-PED-2016-0924 (DEV-TREC) and PN-III-P4-ID-PCE-2016-0270 (OLFA-ROA) Projects. European Union's Horizon 2020 research and innovation programme through the EUROCHAMP-2020 Infrastructure Activity under grant agreement No. 730997 and is also gratefully acknowledged.

96. KINETICS AND PRODUCT DISTRIBUTION OF THE GAS PHASE REACTIONS OF β - OCIMENE AND CAMPHENE WITH Cl ATOMS AT ROOM TEMPERATURE

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Abstract

β -Ocimene and camphene are monoterpenes, which emissions has been detected from several types of vegetation (1-3). In the troposphere, biogenic volatile organic compounds (BVOCs) can react with the main atmospheric oxidants (OH radicals, NO₃ radicals and O₃ molecules) leading to the formation of variety groups of product species and participate in the formation of tropospheric ozone and secondary organic aerosols (4). In this study, the rate coefficients for the gas-phase reaction of Cl atoms with β -ocimene and camphene were measured using the relative rate method at 298 K and 760 Torr. The experiments were performed in a long-path atmospheric chamber coupled to Fourier transformed infrared spectroscopy. The obtained rate coefficients are $k(\beta\text{-ocimene} + \text{Cl}) = (5.5 \pm 0.9) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{camphene} + \text{Cl}) = (3.2 \pm 0.5) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. In addition, products identification has been performed at 298 K and 760 Torr in the absence of NO_x using an 80 L collapsible Teflon chamber with Gas-Chromatography and Mass Spectrometer. In order to identify carbonyl products, the samples for each studied reaction were derivatized on fiber using the SPME technique and PFBHA as derivatizing agent. For the reaction of β -ocimene with Cl atoms, acetone was positively identified as reaction product. Acetone and formaldehyde were identified as reaction products for the reaction of camphene and Cl atoms. The branching ratios for the addition of Cl atom to the structures of the studied monoterpenes have been estimated through a theoretical calculation using M06/cc-pVTZ and CBS-QB3 functions. Mechanisms are proposed and atmospheric implications are discussed.

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97. MORPHOLOGY AND REACTIVITY: A DFT STUDY ON CURVED GRAPHENE

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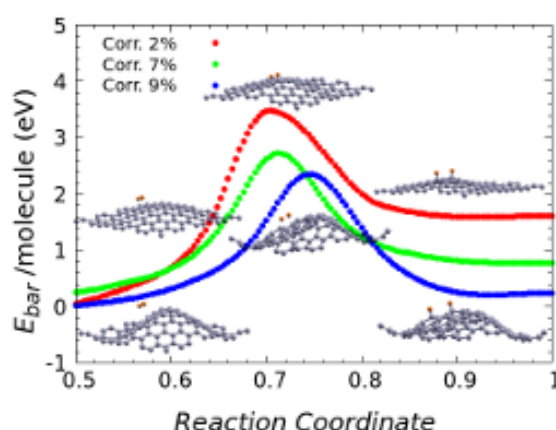
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Abstract

Graphene's strength and extreme flexibility allow sustained ripples in a wide range of amplitudes and wavelengths. Ripples modulate local curvature, which is strongly correlated with the stability of chemisorbed hydrogen atoms [1]. Curvature induced local pyramidalisation, i.e. pushing a carbon site towards the sp³ configuration, contributes to the increase of its reactivity. Thus, the functionalization of curved graphene with hydrogen, or other adatoms, gives the possibility to tune its chemical and adsorption properties for diverse applications [2,4].

In this work, we address the H₂/graphene interaction for the general understanding of graphene morphology/reactivity relationship. We propose that curvature manipulation could be used to improve the adhesion kinetics and perform a systematic DFT based study to evaluate the dependence of chemi(de)sorption barriers on curvature. Model systems are those with varying levels of corrugation, generated by lateral compression of the isolated graphene sheet and chosen to approximate the symmetry of natural rippling of graphene grown on SiC.



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98. STRUCTURE-REACTIVITY TREND FOR THE OZONOLYSIS OF FATTY ACID MONOLAYERS – A MOLECULAR DYNAMICS PERSPECTIVE

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Abstract

The investigation of surfactant monolayer kinetics by means of vibrational sum frequency generation (VSFG) spectroscopy [1] grants insights into the reactive processes occurring at coated aerosol- or water-air interfaces. The chemical properties of such monolayers have an impact on the oxidation capacity of the atmosphere, change the hygroscopicity of the aerosol droplets and their ability to act as a cloud condensation nuclei, and facilitate the release of partially oxidated organic compounds into the gas phase.

VSFG experiments have indicated a trend in the second-order rate constants of the ozonolysis at various unsaturated cis-fatty acid monolayers. For dense monolayers in the liquid-condensed phase, the reactivity increases in the following order: petroselinic acid (PA, D6), oleic acid (OA, D9), vaccenic acid (VA, D11) and 21-docosenoic acid (DA, D21), [2] and hence is a function of the double bond position in the alkyl chain. Moreover, it has been reported that the reactivity is also dependent on the surface concentration. [3] However, interpretation of the obtained experimental results in terms of the rate-determining thermodynamic and dynamic effects, both related to the structure of the monolayer, turns out to be challenging.

All-atom molecular dynamics simulations of the surfactant-coated interfaces may help to develop an understanding on the microscopic level. Monolayers of fatty acids at the water-air interface were theoretically investigated as model systems. The CHARMM-c36 lipid force-field [4] was used to simulate monolayers of selected fatty acids at different surface concentrations relevant to the performed VSFG experiments. The surface concentrations for the fatty-acid boxes were chosen to include liquid-condensed, liquid-expanded and gaseous monolayers. Reaction rates of the ozonolysis are discussed with respect to the structural parameters of the monolayers, e.g. local densities evaluated as Voronoi volumes of molecular groups, tilt angles and accessible surfaces of the double bond or radial distribution functions (RDFs) of the fatty acids.

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101 PHOTOCHEMISTRY OF (FCO)₂ AT 266 nm. UV AND IR EMISSION

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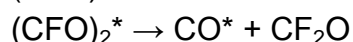
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Abstract

Oxalylfluoride has an allowed electronic transition $\hat{A}1 \text{ Au} \leftarrow X1 \text{ Ag}$ located at about 308 nm. For excitation above this energy photochemical decomposition takes place. In the present work we explore the luminescence and photodissociation at 266 nm in the presence of different quenchers.

Photolysis was initiated with a quadrupled Nd:YAG at 266 nm (0,4 W). IR radiation was collected with a concave golden mirror and focused through a filter (2000 – 2400 cm⁻¹) into an InSb detector. To register the UV-Visible luminescence, a monochromator connected to a photomultiplier was used.

Under the experimental conditions, several processes may occur:



The luminescence spectrum is presented in Figure 1a. We've chosen the band at 356.7 nm to register the temporal decay of the $\hat{a}3\text{Au}$. In the presence of Ar only a decrease in life-time was observed, whereas in the presence of more complex molecules (CO, CH₃C≡N and cyclohexane) an increase in luminescence takes place concomitant with the increase in pressure. Figure 1b. presents the time-resolved luminescence at different pressures.

Figure 1c. presents the FTIR spectrum of the final products of photolysis. With the IR filter, only the CO* emission is measured. Figure 1d. presents the time-dependence of the IR emission bands. No pressure dependence was observed when Ar is loaded, but the IR signal decreases drastically with the increase in pressure of the "complex molecules".

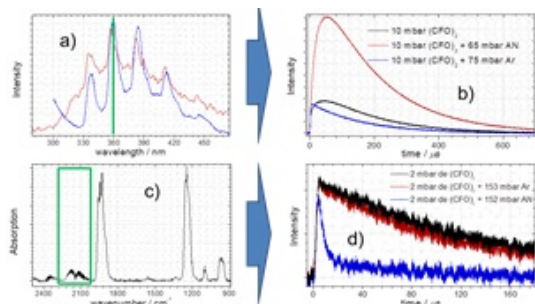


Figure 1. a) Emission of (FCO)₂ pumped with a Nd:YAG 266nm (red line) and stationary emission (blue line). b) temporal decays of the band at 356.7 nm at different pressures. c) IR spectrum of the products of the photodecomposition. d) temporal decays of the bands 2000 – 2400 cm⁻¹.

102. PHOTOLYSIS OF METHYL FORMATE AT 248 nm, A STUDY ON THE VIBRATIONAL RELAXATION OF CO.

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Abstract

A previous work on the photolysis of HC(O)OCH₃ at 248 nm by Lombardi et al [1] suggests that the so-called roaming mechanism is involved in the production of a percentage of the CO product. This implies that after the intramolecular abstraction of the H atom, the CH₃OH will be formed with high vibrational energy in the OH-stretching mode, leaving a CO co-fragment with low rotational and translational energy which is known as the typical roaming signature. If roaming were involved as one of the main paths, it would be expected to observe a bi-modal distribution on the rotational energy for the lower v levels of CO.

We acquired time-resolved FTIR emission spectra of CO in the region of 1800-2200 cm⁻¹ at a spectral resolution of 0.3 cm⁻¹, working at low pressures to minimize the effects produced by collisions. This, together with the improvement in the signal to noise ratio with respect to the one achieved by Lombardi et al, allowed us to analyze the emission spectra of CO in much greater detail, obtaining information of the emission from vibrational levels up to 9 in contrast to the previous report that only analyzed emission up to $v=4$. After performing a careful analysis, we derived results significantly different from those previously reported under similar experimental conditions [1]. The CO appears to follow a Boltzmann distribution, with no evidence of a bimodal distribution for any of the analyzed vibrational levels. No emission from the stretching mode of the OH in the CH₃OH was observed as expected if roaming mechanism were one of the major channels. We also estimated the branching ratios of all the possible reactions forming CO derived from the calculated PES with the CCSD(T)/Aug-cc-pVTZ/WB97X/6-311++g (3df, 2p) method finding that the main reaction occurs through TS1 with a branching ratio of 0.73. In addition, we derived the first energy balance for the photolysis of HC(O)OCH₃ at 248 nm, obtaining a rotational energy of 3.3 kJ mol⁻¹ and a vibrational energy of 73 kJ mol⁻¹.

Our experimental results are concluding and together with the aid of theoretical calculations we conjecture that the observed emission of the CO fragment is originated from the minimum energy path that involves a transition state TS1. No evidence of roaming has been found with this experimental technique.

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103. SELF QUENCHING OF NO($A^2\Sigma^+$): EVIDENCE FOR THE FORMATION OF NO($A^4\Pi$)

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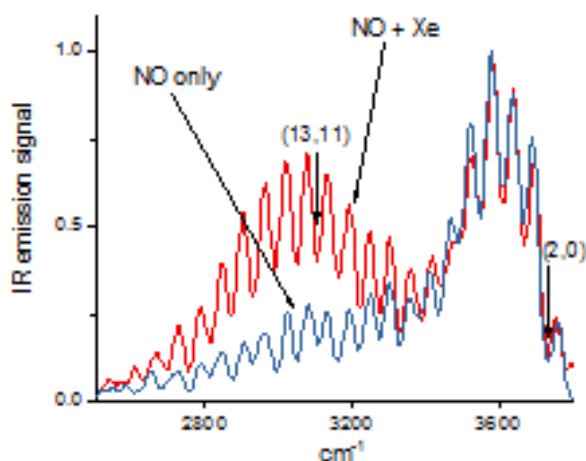
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Abstract

The self quenching of NO($A^2\Sigma^+$ $v=0$) has been studied by fast time resolved observations of the formation of vibrationally excited ground state molecules NO($X^2\Pi$, v). As well as direct ground state formation on the time scale of the A state lifetime (*ca.* 200 ns) we see a delayed contribution particularly in high vibrational levels, the rate of increase of which depends linearly upon NO pressure. A dramatic time dependent effect occurs in the presence of Xe, where a population inversion in the high vibrational levels is seen: an overtone ($\Delta v=-2$) emission spectrum near 3200 cm^{-1} , shown in Figure 1, illustrates the high vibrational levels (near $v=13$) preferentially formed in the presence of Xe. Xe does not quench the NO(A) state on the time scale of these observations, and the evidence points to a precursor state of the high vibrational level populations produced collisionally. The only energetically possible precursor that explains the results is NO($a^4\Pi$) and we propose that self quenching of NO($A^2\Sigma^+$) forms both NO($X^2\Pi$) and NO($a^4\Pi$) state in spin allowed steps, that additional vibrationally excited ground state NO is formed by rapid self quenching of NO($a^4\Pi$) and that an inverted vibrational distribution (similar to that expected from Franck Condon overlap of the a and X states) is formed from slower quenching of NO($a^4\Pi$) in a spin forbidden step by polarisable Xe. Rate constants and quantum yields will be presented for the behaviour of the kinetically elusive NO($a^4\Pi$) state.



104. THEORETICAL STUDY FOR THE REACTION BETWEEN HYDRAZINE DERIVATIVES WITH OH

N. Kanno*

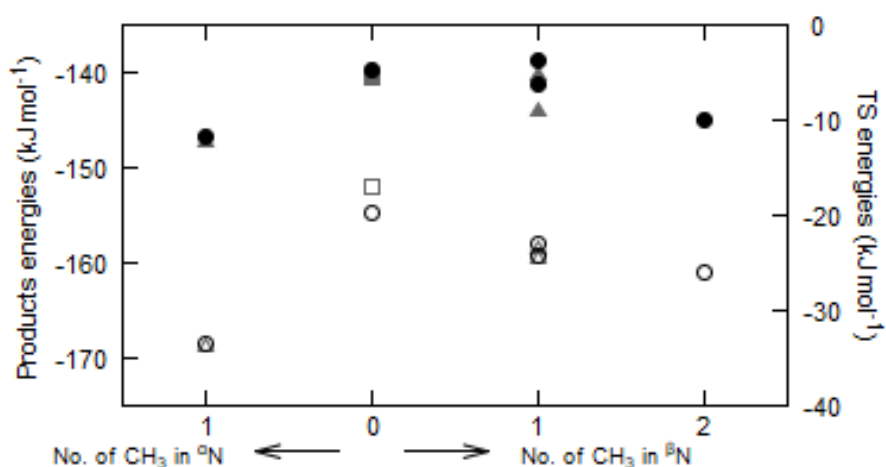
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Abstract

Hydrazine and its methyl derivatives are widely used fuels for space craft rocket thrusters. Vaghjani experimentally reported OH reactions with these compounds and suggested that the reaction rates were enhanced with increasing methyl substitution numbers and showed slightly negative dependence on temperature [G. L. Vaghjani, IJCK, 33, pp. 354-362 (2001)]. In the present study, the titled reactions have been theoretically investigated.

Following figure shows products (open plots) and transition states (solid plots) energies for H abstraction reactions from amino group, i.e. ${}^{\alpha}\text{NHX}^{\beta}\text{NYZ} + \text{OH} \rightarrow {}^{\alpha}\text{NX}^{\beta}\text{NYZ} + \text{H}_2\text{O}$ (X, Y, Z = H or CH₃), calculated at the CBS-QB3// ω B97X-D/6-311++G(d,p) level of theory. The calculated energies (circles) were in good agreement with previous theoretical values of N₂H₄ (boxes [D. A. Armstrong et al., JPCA, 101, pp. 4761-4769 (1997)]) and those of CH₃NHNH₂ (triangles [H. Sun et al., JPCA, 116, pp. 5045-5056 (2012)]). Both the products and transition states energies were decreased with increasing the number of substituted methyl groups. The substitution effects in ${}^{\alpha}\text{N}$ were found to be larger than those in ${}^{\beta}\text{N}$. Due to the formation of pre-reaction complexes, the calculated transition states energies were lower than those of reactants, except for the H abstraction from methyl groups, supporting the negative temperature dependence of the rate coefficients observed in the previous experiment.



105. STUDYING REACTION OF N⁺ IONS WITH HD USING RF 22 POLE TRAP DOWN TO 15 K.

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Abstract

Low-temperature studies of ion-molecule reactions may provide us with important information for understanding the processes in interstellar space. For example, reaction of nitrogen ions with hydrogen is important for astrochemistry as can be the reaction leading to ammonia production in the interstellar medium. Studies of reaction N⁺ with H₂(J) did not show whether the activation energy was purely due to the endoergicity or an energy barrier contributed as well. Thus, studying the isotopic variant can be helpful to solve the problem with a pathway of N⁺ with H₂(J) interaction. In addition, the results of our measurements will be compared with phase space theory calculations.

The reaction of N⁺ ions with molecular HD will be compared with previous experimental results in which used various experimental techniques such as guided ion beam, selective ion flow tube or supersonic expansion in temperature range from 200 K to 300 K. Our linear rf 22 pole ion trap allows us to measure at temperatures and pressures relevant to the interstellar diffuse clouds. We will present study of the reaction rate coefficients at temperatures down to 15 K. The rate coefficient has constant value $3.8 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at temperatures from 250 K to 50 K and then it decreases to $1 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at 15 K.

Acknowledgments: We thank the Technical University of Chemnitz and the DFG for lending us the 22-pole trap instrument and Dieter Gerlich for discussion. This work was supported by GACR 17-19459S, GACR 17-18067S, GAUK 1584217, GAUK 1168216 and GAUK 1144616.

106. THREE-DIMENSIONAL MASTER EQUATION (3DME) APPROACH

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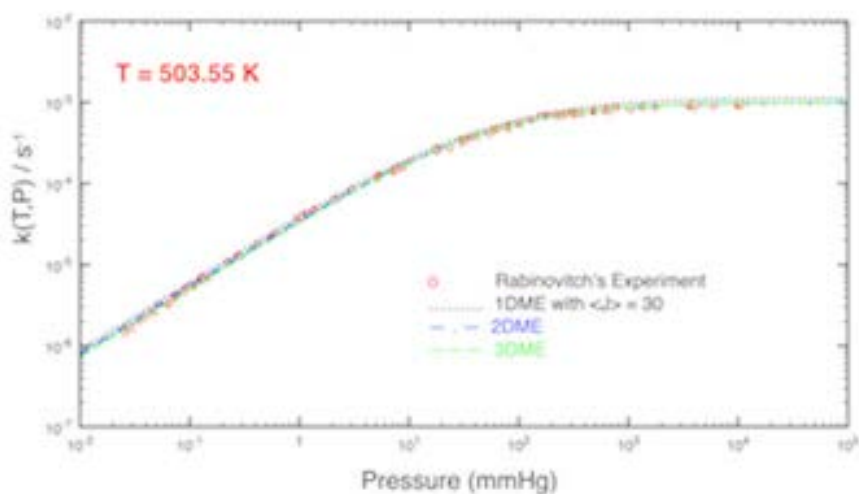
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Abstract

The master equation technique is a basic tool to interpret gas-phase experimental results and to provide phenomenological rate coefficients for modeling. For some reactions where there are significant changes of rotational constants along the reaction coordinate, including effects of angular momentum explicitly into a master equation model is a necessity. While the total angular momentum J is always conserved, its projection (the K quantum number) is not. Therefore, the convolution of external rotational quantum states with vibrational quantum states depends on how K is treated: as either adiabatic or active. Because of these, there are, in principle, four different models that can be used to compute microcanonical rate constants: (i) first, model-I assumes that K is active for both TS and reactant; (ii) second, model-II uses K adiabatic for both TS and reactant; (iii) third, model-III applies K active to TS, but K adiabatic to reactant; and (iv) final, model-IV assigns K adiabatic to TS, but K active to reactant. Model-I will result in a 2DME approach, whose solutions have been reported (by us) recently. The remaining models will lead to a 3DME, whose solutions will be given here for the first time. In this work, we have developed an algorithm for pragmatic solutions of 3DME using model-II. Two examples (one is for an isomerization of CH_3NC to CH_3CN (Figure 1); and the other is for a dissociation of NH_3 to $\text{H} + \text{NH}_2$) will be discussed. In addition, comparison of 3DME results with those of 1DME and 2DME will also be presented.



107. HIGH ACCURACY OH REACTION RATE CONSTANT MEASUREMENTS: STUDIES OF PRESSURE DEPENDENCIES

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Abstract

The accuracy of OH kinetic data is of primary importance for the comprehensive modeling of any compound's atmospheric behavior and of its environmental impacts, such as its atmospheric residence time and its potential roles in stratospheric ozone depletion, global warming, and local pollution.

Rate constants of OH reactions with hydrocarbons and halogenated hydrocarbons can now be determined with an accuracy of 2-3% over the temperature range 220 K to 370 K. This has been demonstrated in studies of OH reactions with various halogenated and non-substituted organics including alkanes, alkenes, alcohols, and ethers. Lower data scattering and higher measurement accuracy allow for rigorous statistical analysis of the results and can reveal often-missing details about the reactivity, such as the (small) dependencies of the rate constant on the temperature, pressure, and reactant molecular structure. Such details include the

- temperature dependence of both H-abstraction and OH-addition reactions exhibiting a noticeable curvature in the Arrhenius plot that cannot be attributed to experimental artifacts,
- determination of substantially different reactivities and their temperature dependencies as well as IR absorption spectra for the stereoisomers of unsaturated compounds,
- determination of the temperature dependencies of OH-addition rate constants that are approaching the collision frequency.

Recently, we expanded the pressure range of experiments to allow OH kinetic measurements between 3 Torr to 900 Torr. Along with high accuracy of the data this allows

- determination of both low-pressure and high-pressure limiting rate constants from data obtained over a limited pressure range including an effect of different inert bath gases,
 - observations of unexpected pressure dependencies for OH-addition reaction rate constants (such as in case of C4 alkenes), and
- observation/quantification of side chemical reactions such as OH regeneration, which can affect the results of accurate rate constant measurements.

This presentation will provide examples of several of these measurement results that were recently obtained in our laboratory including higher accuracy data for OH reactions with ethylene, fluorinated ethylenes, and larger alkenes.

108. AMINOSILANES FROM CO-PYROLYSIS OF SILANE AND AMMONIA

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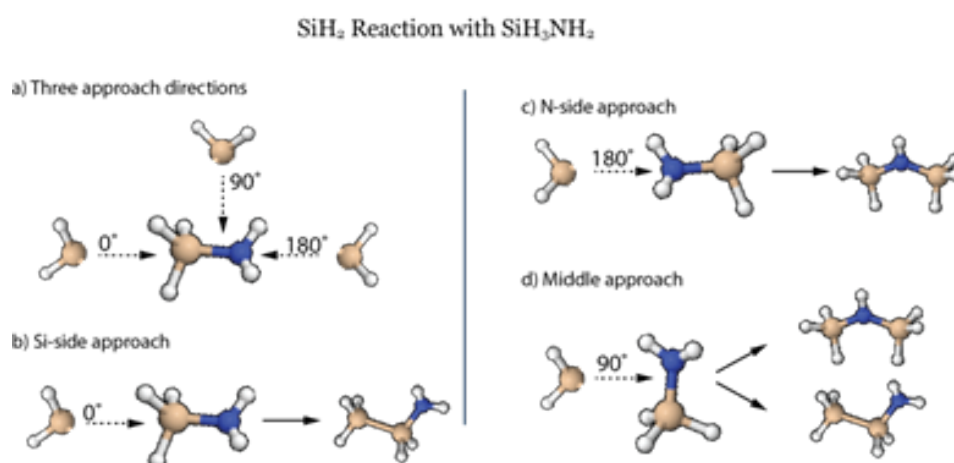
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Abstract

Small silicon nitride molecules are building blocks on the route to larger, extended silicon nitride systems. Building these systems from the bottom up offers a chance to control their stoichiometry, and thus also control other properties. Co-pyrolysis of silane and ammonia can do just that; it leads to a variety of silicon-nitrogen hydrides. Under our target synthesis conditions of about 700 K and 1 atm, the number of species and pathways are myriad. For electronic structure calculations, we use density functional theory with density-fitted integral approximations for gradient calculations and then a density-fitted local coupled cluster method with an explicit electron correlation for energy calculations. The method faithfully produces properties of known species in the system and it is also tractable for larger molecular systems. A typical radical in the reaction soup during pyrolysis is silylene, SiH_2 . The figure shows an example result of our calculations, indicating that the angle of attack of SiH_2 on silylamine affects which bimolecular product is formed. In this contribution, we present further results about larger species that appear in this co-pyrolysis. These new calculations give hints on how to steer a real reactor to favor production of either silicon-heavy or nitrogen-heavy species. We cast these results forward to lead our experimental campaigns of producing silicon nitrides in our lab- and pilot-scale reactors.



109. CATALYTIC OXIDATION OF CO ON PERFECT AND DEFECTIVE CUO AND CU₂O SURFACES

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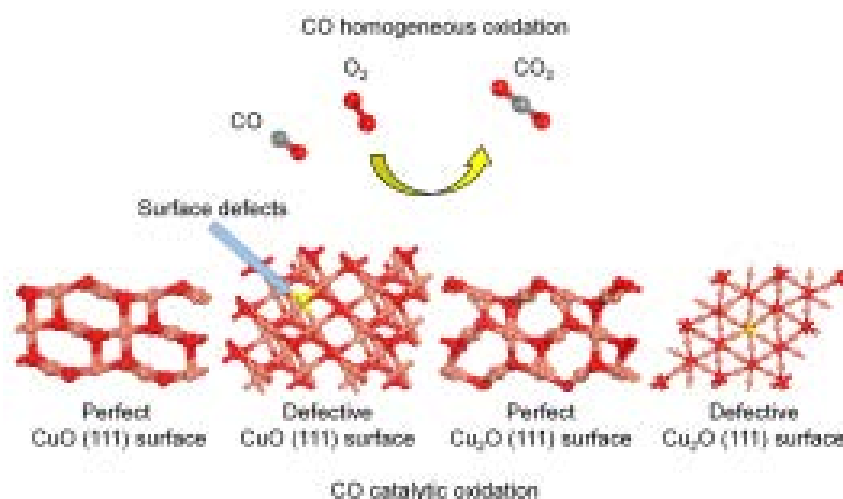
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Abstract

Catalytic removal of CO is important for the wellness of human beings and the environment. CuO and Cu₂O are regarded as promising candidates for cost-efficient CO abatement catalysts, and, therefore, a good command of the surface chemistry is of significance for their design and applications. The mechanism of CO oxidation on CuO and Cu₂O surfaces were theoretically explored using density functional theory calculations. Both the perfect and defective CuO and Cu₂O surface electronic properties were obtained. The adsorption, reaction and desorption processes of CO oxidation on CuO and Cu₂O surfaces were studied. CO oxidation mechanisms were proposed taking into account the Mars-van-Krevelen, Langmuir-Hinshelwood and Eley-Rideal type reaction routes. Kinetic modeling was obtained with their elementary reaction rate constants provided in Arrhenius form. The effect of surface deficiencies was discussed in detail to illustrate their effect on CO oxidation processes. The obtained results could be helpful for the development of Cu-based CO abatement catalysts.



110. KINETICS OF THE REACTIONS OF ETHYL, n-PROPYL, AND n-BUTYL RADICALS WITH MOLECULAR OXYGEN

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Abstract

Reactions of carbon-centered radicals with molecular oxygen are important in atmospheric and combustion chemistry. We have experimentally studied the kinetics of these reactions of ethyl, n-propyl and n-butyl radicals at low pressures (0.2 – 6 Torr) and at temperatures relevant to atmospheric and low-temperature combustion chemistry (190–710 K). The purpose of the study is also to compare the pressure and temperature dependent $R+O_2$ rate coefficients for the simplest n-type alkyl radicals. Extensive experimental data are available for methyl+ O_2 (Fernandes, R. X.; Luther, K.; Troe, J., JPC A, 110, pp 4442–4449 (2006)) and ethyl+ O_2 reactions, (Fernandes, R. X.; Luther, K.; Marowsky, G.; Rissanen, M. P.; Timonen, R. S.; Troe, J., JPC A, 119 (28), pp 7263–7269 (2015)) whereas data for n-propyl and n-butyl are more sparse.

The measurements were performed under pseudo-first-order conditions (excess O_2) in a tubular laminar flow reactor. Pulsed excimer laser photolysis (193 nm or 248 nm) was used for radical production and a photoionization mass-spectrometer for the time-resolved radical detection.

The results of our experiments can be used to generate falloff curves for the $R+ O_2$ addition reaction and to fit different master equation models to them. The results also show how the length of an n-type alkyl radical affects its reactivity with oxygen. We will compare our measured results to other author's experimental and theoretical results at the meeting showing the measured bimolecular $R+ O_2$ rate coefficients of three n-type alkyl radical as a function of bath gas density at few temperatures and the lines corresponding to modeled falloff curves.

111. ISOTOPIC EFFECTS IN THE INTERACTION OF D_2O^+ WITH H_2 AND D_2 AT LOW TEMPERATURES

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Abstract

Hydride ions, commonly detected in the interstellar medium (M. Gerin et al., *A&A*, 518, L11 (2010), F. Wyrowski et al., *A&A*, 518, A26 (2010)), can be involved in water production in interstellar space. As a follow-up to our recent study of a reaction $H_2O^+ + H_2 \rightarrow H_3O^+ + H_2$ (T. D. Tran et al., *ApJ*, 854(25), (2018)), we decided to study isotopic variations of the reaction.

The rate coefficient k_{H_2} of the reaction $D_2O^+ + H_2 \rightarrow D_2HO^+ + H$ and the rate coefficient k_{D_2} of the reaction $D_2O^+ + D_2 \rightarrow D_3O^+ + D$ have been measured using a 22-pole radiofrequency ion trap apparatus in the temperature range 15 – 300 K and 15 – 200 K, respectively.

During evaluation of results of the $D_2O^+ + H_2$ rate measurements, we considered the second channel $D_2O^+ + H_2 \rightarrow DH_2O^+ + D$. We assume that an upper limit for the second channel is 4%. At high temperatures, the DH_2O^+ production is also caused by the reaction with water molecules. It has to be mentioned that the isotopic exchange has not been observed.

The coefficients k_{H_2} , k_{D_2} of both reactions are nearly constant in the studied temperature range. Moreover, the value of k_{D_2} is approximately one third lower than the value of k_{H_2} . The lower value of k_{D_2} was expected due to a higher mass of D_2 .

Acknowledgments: We thank the Technical University of Chemnitz and the Deutsche Forschungsgemeinschaft for lending the 22-pole ion trap instrument and professor Dieter Gerlich for discussion. This work is partly supported by GACR Grant No. 17-19459S and 17-18067S, by GAUK Grant No. 1584217 and 1168216.

112. DETAILED REINVESTIGATION OF WATER NUCLEAR SPIN CONVERSION KINETICS IN SUPERSONIC EXPANSION

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Abstract

Molecules with multiple identical nuclei often exist in several distinguishable nuclear spin isomers. Specifically, H₂O has two isomers with total nuclear spin $I=0$ (Para) and $I=1$ (Ortho) respectively. Processes in which one isomer is transformed to other (nuclear spin conversion) have been studied for several small polyatomic molecules such as NH₃, methane, and its derivatives. In the gas phase it has generally been observed that kinetics of the spin conversion is slow as the process is symmetry forbidden in binary collisions.

Rapid cooling in supersonic jet expansions creates significant Ortho-Para non-equilibrium and thus provides convenient tool to study the conversion process. As a general trend it has been found, that the nuclear spin is conserved on the time scale of the expansion. Notable exception from this behavior has been reported by Manca Tanner and Quack [1] in the case of supersonic expansion of H₂O seeded in Ar buffer gas. They observed fast conversion kinetic rates as deduced from spectroscopic measurements and attributed the observation to cluster formation in the expansion. The effect has however been subject to several subsequent experimental studies with somewhat contradictory conclusions [2].

In this contribution we report recent re-investigation of the water nuclear spin relaxation in supersonic jet expansion with significantly bigger data set and modified approach to analysis to avoid possible sources of systematic errors present in previous studies. Specifically, by sampling the three lowest rotational states for both Ortho and Para nuclear spin isomers we determine the absolute Ortho/Para population ratios and local expansion rotational temperatures with much higher accuracy than was possible previously. We also explore a wide range of expansion conditions to map the onset of cluster formation in the expansion and quantitatively compare the Ortho/Para ratios under both clustering and non-clustering conditions. In agreement with our previous preliminary measurements we conclude that the nuclear spin conversion is not observed under our experimental conditions.

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113. OXYDATION OF A POTASSIUM IODIDE SURFACE BY GASEOUS OZONE

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Abstract

Reactive halogen species play an important role in tropospheric chemistry, especially in the polar and marine boundary layers. They impact the oxidative capacity of the troposphere via catalytic destruction of ozone or altering NO/NO₂ and OH/HO₂ cycles. Because of the large surface areas of aerosol clouds, their role in the atmospheric chemistry is crucial. Although iodine species are a minor constituent of seawater, recent field studies have measured significant levels of organic and inorganic iodine in the marine boundary layer (Huang et al. Geophys. Res. Lett. 37 (2010) L03803). In order, to better understand the heterogenous processes that take place on marine aerosols, we modeled the interaction with atmospheric photo-oxidant such as ozone.

For example, experimental studies of ozone on a dry (100) KI leads to the formation of a passivation layer of KIO₃. This reaction initiates at step edges of the surface first and then spreads across the terraces (Brown et al. J. Phys. Chem. C 112 (2008) 5520-5525 ; Brown et al. J. Phys. Chem. C 112 (2008) 5520-5525). Surface adsorbed water molecules induce a completely different reaction pathway that leads to the formation of gaseous iodide compounds (Brown et al. J. Phys. Chem. C 114 (2010) 14093-14100).

In this context, the aim of our study is to gain more knowledge on the heterogeneous processes of solid surfaces with gas-phase reactants. We describe here the successive reaction steps that lead to the formation of potassium iodate KIO₃ at the KI surface at dry conditions. We compare geometries and reaction energies of different reaction sites at step edges and terraces. We will also present the transition state of the first stage of the oxydation reaction at some of these sites. Molecular simulations have been performed using the Vienna Ab initio Simulation Package (VASP).

114. AQUEOUS-PHASE OXIDATION OF THE MONOTERPENE SECONDARY ORGANIC AEROSOLS (SOAS)

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Abstract

In the work presented, kinetics and mechanisms of aqueous phase oxidation of the semi-volatile oxidation products of α -pinene and limonene were investigated. (Witkowski and Gierczak, Environmental Science & Technology, 51, 9765-9773, (2017) , Witkowski et al., Environmental Science & Technology, (2018)) The aim of this project is to provide insights into aqueous-phase processing of monoterpene secondary organic aerosols (SOAs). Aqueous-phase oxidation by hydroxyl radicals (OH) was studied for *cis*-pinonic acid and for the twenty compounds that contribute to limonene SOA. (Witkowski and Gierczak, Atmospheric Environment, 154, 297-307, (2017)) A significant fraction of the first-generation oxidation products of limonene retain the less reactive, (Leungsakul et al., Environmental Science & Technology, 39, 9583-9594, (2005)) exocyclic double bond. (Nørgaard et al., Journal of The American Society for Mass Spectrometry, 24, 1090-1096, (2013)) Consequently, these unsaturated compounds can react with ozone (O₃), in addition to the reaction with OH in the aqueous-phase. The bimolecular rate coefficients obtained for the reaction of monoterpene carboxylic acids with OH were: 2-3 × 10⁹ M⁻¹s⁻¹ for the saturated compounds (including *cis*-pinonic acid) and 5-20 × 10⁹ M⁻¹s⁻¹ for the unsaturated oxidation products of limonene. (Witkowski et al., Environmental Science & Technology, (2018)) Bimolecular rate coefficients calculated for the aqueous-phase ozonolysis of the unsaturated limonene acids were between 2-10 × 10⁴ M⁻¹s⁻¹. In fogs and clouds with LWC = 0.3-0.5 g × m⁻³, semi-volatile compounds that contribute to monoterpene SOA will reside entirely in the aqueous-phase. Consequently, aqueous-phase processing of the monoterpene SOA should be relevant under realistic atmospheric conditions assuming that [OH] ≈ 2 × 10⁻¹⁴ M and [O₃] ≈ 2 × 10⁻⁹ M. (Herrmann et al., Chemical Reviews, 115, 4259-4334, (2015)) Moreover, products of the investigated aqueous-phase reactions were identified as low-volatility, highly-oxygenated compounds. (Witkowski and Gierczak, Environmental Science & Technology, 51, 9765-9773, (2017) , Witkowski et al., Environmental Science & Technology, (2018)) These results indicate that aqueous-phase oxidation of monoterpene SOA may lead to aqueous-phase SOA (aqSOA) in the atmosphere.

115. VOLATILE ORGANIC COMPOUNDS AND SECONDARY ORGANIC AEROSOLS FROM SOIL AMENDMENTS: LABORATORY AND FIELD COMPARISON

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Abstract

The emissions of volatile organic compounds (VOC) from plants have been studied for decades; in contrast, VOC from soil or related to agricultural practices have received far less attention even though recent studies suggest that they represent important sources of VOC¹. It has been showed that under certain conditions and for specific ecosystems, VOC emissions from soil could reach the same order of magnitude as canopy emissions¹. While NH₃ is quantitatively the largest emission from agriculture, many other agricultural air pollutants are also of environmental concern, including reactive N and S species, VOC and aerosols. These gases and aerosols emissions occur from agricultural practices including confined animal feeding operations, crop production or amendments application.

Organic waste products (OWP) are used in agriculture as organic amendments to improve soil fertility. The valorization of OWP is currently promoted as a substitute for mineral fertilizers. OWP have different characteristics due to their origin and the treatments they undergo before spreading. There are few studies quantifying the VOC from OWP, and those studies primarily address their odorant properties for identifying odor abatement techniques³. These studies have quantified hydrocarbons VOC, S, N and oxygenated compounds³.

The aim of this study is to investigate VOC emissions from agricultural soils amended with different OWP. Their subsequent reaction with O₃ and the formation of secondary organic aerosols (SOA) are characterized. The experiments are performed in an atmospheric chamber coupled to an aerosol flow tube. Physical and chemical characterization of VOC and SOA is performed by on-line and off-line analysis.

Preliminary results showed that the reaction of O₃ with the VOC emitted by a green waste compost lead to SOA formation, while the liquid manure showed no SOA. The gas phase and aerosol measurements showed the emission and formation of a majority of VOC and oxygenated hydrocarbons.

The results of this study could help us gain a better understanding of the impact of agriculture on atmospheric VOC and SOA. However, the results from this laboratory-based study cannot be fully used to predict the specific VOC and SOA emission rates; thus field studies are now conducted on the VOC and SOA emissions from different OWP spread on an agricultural ICOS field in France.

116. ATOMIC CHLORINE GENERATION USING A RADIO-FREQUENCY ATMOSPHERIC PRESSURE PLASMA FOR USE IN THE COMPARATIVE REACTIVITY METHOD

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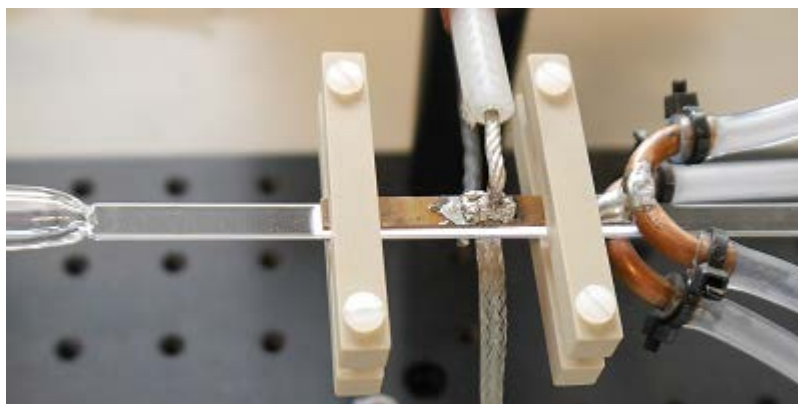
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Abstract

Highly reactive atomic chlorine is important in the kinetics of atmospheric chemistry. However it is difficult to measure directly due to the small concentrations present. This makes absolute measurements in the field troublesome. One such method is the comparative reactivity method (CRM) which has already been used in Suriname, Mainz and Paris to measure OH radical reactivity (V. Sinha et al., *Atmos. Chem. Phys.*, vol. 8, no. 8, pp. 2213-2227, 2008., C. Dolgorouky, et al., *Atmos. Chem. Phys.*, vol. 12, no. 20, pp. 9593-9612, 2012.). This work aims to use a radio-frequency atmospheric pressure plasma source to produce the atomic chlorine for the CRM to measure atomic chlorine reactivity. A plasma is used due to the increased conversion rates they offer compared to current mercury vapour lamps (J. P. Booth et al., *J. Phys. D.*, vol. 45, no. 19, pp. 195201, 2012.) and in doing so decrease chemical inferences from molecular chlorine.

The plasma source itself is a dielectric barrier discharge; it consists of a rectangular borosilicate capillary with two copper electrodes clamped on the outside. One of the electrodes is grounded while the other is connected to a 40.68 MHz power supply, connected in series with an impedance matching network. A total flow rate of 1.5 slm of a mixture of argon and chlorine is used with a typical mixing ratio of 1000:1. The outlet of this capillary is connected to a cylindrical glass reactor vessel.



117. TOWARDS DIRECT MOLECULAR ANALYSIS OF ATMOSPHERIC OXIDIZED MERCURY

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Abstract

Mercury is a persistent environmental pollutant arising from both anthropogenic and natural sources. Gaseous oxidized mercury (GOM) is significantly more water soluble than elemental Hg and should be the main form responsible for deposition into environmental sinks, however, the formation mechanisms and speciation of GOM are poorly understood due to its relatively low concentrations and labile nature. We investigated ion-molecule chemistry of gas-phase HgCl_2 with SF_6^- , CO_3^- , CO_4^- and $\text{NO}_3^-\text{HNO}_3^-$ reagent ions by ion-drift chemical ionization mass spectrometry as a mechanism for detection via charge transfer in mass spectrometry. DFT and ab-initio computations coupled with rate constant calculations based on average dipole orientation (ADO) theory were used to understand and elucidate reaction pathways and corroborate experimental results. We found that the reaction of HgCl_2 with SF_6^- , CO_3^- , CO_4^- and $\text{NO}_3^-\text{HNO}_3^-$ forms $\text{HgCl}_2^+\text{F}^-$, $\text{HgCl}_2^+\text{O}^-$, $\text{HgCl}_2^+\text{O}_2^-$, $\text{HgCl}_2^+\text{CO}_3^-$, $\text{HgCl}_2^+\text{CO}_4^-$, $\text{HgCl}_2^+\text{NO}_2^-$, $\text{HgCl}_2^+\text{NO}_3^-$, and $\text{HgCl}_2^+\text{NO}_3^-\text{HNO}_3^-$, product ions, respectively. These reactions are efficient in converting gaseous oxidized mercury to molecular ions, although competing reactions with O_3 , NO_x , and H_2O may limit their application in atmospheric applications.

Reaction	Rate	$\Delta H_{\text{rxn}}(298\text{ K})$ (kJ/mol/mol)	
	(10^{12} cm ³ /molecule s)	MD6-2XCVTZ	CCSD(T)/AVTZ/MD6-2XCVTZ
$\text{HgCl}_2 + \text{SF}_6^- \Rightarrow \text{HgCl}_2^+ + \text{SF}_6^-$	3.72	-8.32	-8.46
$\text{HgCl}_2 + \text{SF}_6^- \Rightarrow \text{HgCl}_2^+\text{F}^- + \text{SF}_5^-$	5.83	-54.39	-47.80
$\text{HgCl}_2 + \text{O}^- \Rightarrow \text{HgCl}_2^+\text{O}^-$	14.9	-46.61	-49.77
$\text{HgCl}_2 + \text{O}_2^- \Rightarrow \text{HgCl}_2^+\text{O}_2^-$	10.4	-76.79	-74.09
$\text{HgCl}_2 + \text{CO}_3^- \Rightarrow \text{HgCl}_2^+\text{CO}_3^-$	7.95	-71.21	-69.41
$\text{HgCl}_2 + \text{CO}_4^- \Rightarrow \text{HgCl}_2^+\text{CO}_4^-$	7.25	-28.41	-29.48
$\text{HgCl}_2 + \text{CO}_4^- \Rightarrow \text{HgCl}_2^+\text{O}^- + \text{CO}_2$	7.25	+2.83	+19.86

118. DEVELOPMENT OF A MOBILE PHOTOCHEMICAL REACTOR TO INVESTIGATE GAS-PHASE CHEMISTRY AND AEROSOL FORMATION IN THE FIELD

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Abstract

The development of innovative tools is important to tackle atmospheric complexity, i.e. its composition and future changes. Investigating chemical transformations during intensive field campaigns is not straightforward due to the impact of emissions, vertical dilution, and other meteorological parameters on ambient concentrations of trace gases and aerosols. Investigations of these transformations in the laboratory using smog chambers provide a much more controlled environment but are limited to simple chemical systems, which are not representative of complex atmospheres.

The objective of the current study is to combine both concepts through the construction of a mobile photochemical reactor and its deployment in the field during intensive measurement campaigns. This new tool will allow trapping real air masses, directly on site, to characterize the fate of primary emitted trace gases using all the benefits of a smog chamber, i.e. decoupling the chemistry from other processes (emission, transport...). A 9 m³ photo-reactor was constructed to trap ambient air at atmospheric pressure into a FEP foil bag maintained by an aluminium frame. The reactor allows both solar and artificial irradiations, whose irradiance is monitored by a spectroradiometer. The chemical composition, including volatile organic compounds, oxidants and aerosols, is probed in real time during an oxidation experiment using state-of-the-art instrumentation (FastGC/PTR-ToFMS for VOCs, CRM for OH reactivity, PERCA for peroxy radicals, O₃ and NO_x analysers, SMPS for particles). This presentation will describe the photo-reactor setup and its first deployment during the summer 2018 CERVOLAND field campaign.

119. TIME-RESOLVED INFRARED SPECTROSCOPY OF REACTIVE INTERMEDIATES IN ATMOSPHERIC CHEMISTRY: METHOD DEVELOPMENT AND CHARACTERISATION

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Abstract

The behaviour of gas phase reactive intermediates is a key factor in understanding the chemistry of complex systems, and is responsible for controlling atmospheric composition, fuel ignition and processes occurring in interstellar space and star-forming regions. Kinetics of such processes are often studied using flash photolysis techniques coupled to laser-induced fluorescence (LIF) or ultraviolet (UV) absorption spectroscopy, but these techniques are not suitable for all species of interest. While infrared (IR) absorption spectroscopy is a more universal detection method, time-resolved infrared (IR) spectroscopy is less commonly employed to study reaction kinetics of trace species owing to relatively weak IR absorption cross-sections and instabilities in IR laser sources. However, recent developments in mid-IR quantum cascade lasers (QCLs) have led to improved opportunities for sensitive time-resolved IR spectroscopy.

In this work we present the design and characterisation of a new instrument coupling laser flash photolysis to time-resolved infrared quantum cascade laser absorption spectroscopy to determine gas phase kinetics and product yields of reactive trace species. Initial results from an investigation of product yields in reactions of Criegee intermediates will be presented, and directions for future work will be discussed.

120. AN INSTRUMENT FOR TIME RESOLVED HO₂ AND OH MEASUREMENT.

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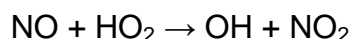
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Abstract

A novel kinetics reactor (Stone et al., RSI, 87, 054102 (2016)) has been used to investigate the OH initiated chemistry of volatile organic compounds, monitoring OH loss and HO₂ formation processes. The reactor can study kinetics over high pressures (tested to >3 bar, N₂/O₂, potentially able to run to 10 bar) and temperatures (295 – 800 K), where the reaction is initiated by flash photolysis (248 nm, 266 nm) of hydrogen peroxide or other suitable precursors.

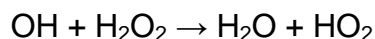
OH loss and regeneration processes were monitored by following the OH radical via off-resonance laser induced fluorescence at 282 nm in the jet-expanded gas, sampled from the reactor via a pinhole. HO₂ formation was monitored by conversion of HO₂ to OH in the low-pressure cell, achieved by addition of a small flow of NO.



After passing through the first detection cell, the probe beam was redirected through the second detection cell, downstream of the NO injection pipe, to sample the OH concentration in this region.

The data from the second cell was then processed to generate HO₂ traces, and fits to these traces provide HO₂ growth rates and HO₂ yields.

The raw HO₂ yields from traces collected from the second cell were compared to the calibration reference reaction to provide accurate yields. The calibration used the reaction of OH with the radical precursor H₂O₂ which directly forms HO₂ with a 100 percent yield.



The reference calibration has been tested against the well-characterized OH + CH₃CH₂OH reaction, where in the presence of O₂, the CH₃CHOH radical is converted to CH₃CHO + HO₂. The measured HO₂ yields are in good agreement with site specific rate coefficients for the production of CH₃CHOH validating the measurement technique.

Results will be presented on OH + n-butanol, where OH recycling kinetics (~500 s⁻¹ at 600 K) and HO₂ yields have been determined over the temperature range 295 – 600 K. In addition, for OH + dimethyl ether + O₂, HO₂ formation kinetics were measured on the 50-500 s⁻¹ time scale at elevated temperatures. Time-resolution of the instrument had no effect on HO₂ yields. The kinetic parameters for the HO₂ growth and OH loss traces from the second cell were perturbed by transport. By comparison to the first cell, for OH + H₂O₂, over a range of removal rates, formation rates up to 1000 s⁻¹ were reliably assigned after correction.

121. APPLICATION OF CHEMICAL ORGANIZATION THEORY TO METHANE COMBUSTION - A NOVEL APPROACH TO IDENTIFY HIERARCHICAL STRUCTURES IN DYNAMICAL COMBUSTION NETWORKS

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Abstract

The theory of chemical organizations has been proposed as a method to study complex reaction networks [1]. It has been successfully applied to various biological networks, for example, to predict growth phenotypes or for checking model consistency [2]. Moreover, a studies showed that it is also useful for complex chemical networks involved of planetary atmospheric photo-chemistries [3]. Here, we present the first application of this theory to combustion chemistry, in particular methane combustion. The first step requires only the reaction network, that is, stoichiometric information without kinetics. The result is a hierarchical decomposition of the reaction network into self-sustaining sub-networks called chemical organizations. A chemical organization is set of molecules that is closed (i.e., no other molecule can be produced) and self-maintaining (i.e., each consumed molecule can be regenerated by the organization) [1]. In our study we could identify a non-trivial decomposition into 62 organization forming a non-trivial hierarchy. From our theorem [1] follows that 131010 combinations of molecular species can not form a steady state; providing already a significant insight into the potential long-term dynamics of the system. In a second step dynamics is included, by projecting a dynamical trajectory (which includes kinetic data) of the combustion process to the lattice of organizations (in a similar way as in Ref. [3]). This provides a fundamentally new perspective of the transient dynamics of the complex combustion process. Software tools for computing chemical organizations for reaction networks are available from the author's website.

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122. DETAILED MOLECULAR NETWORK OF CO₂ HYDROGENATION

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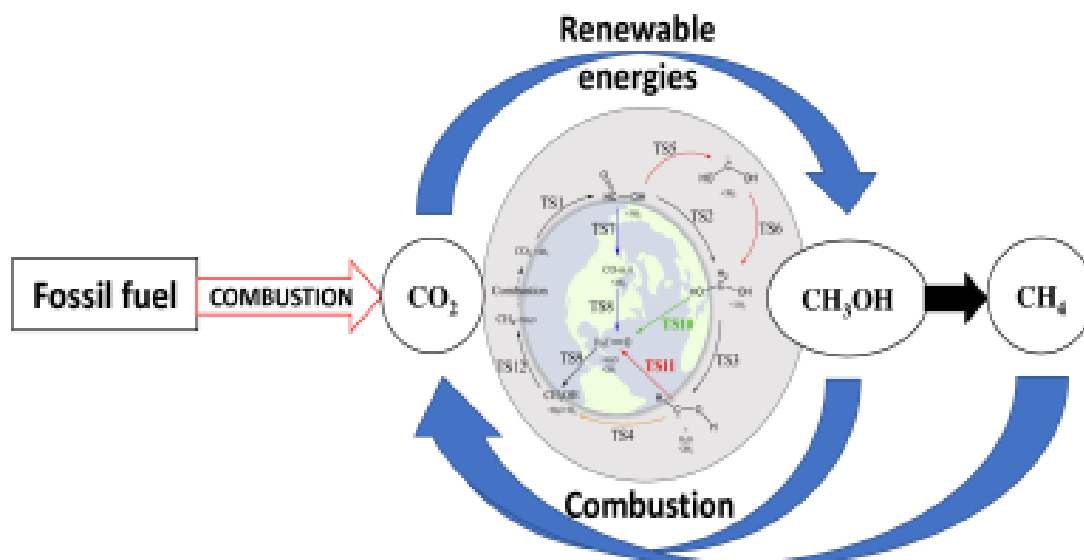
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Abstract

Human usage of fossil fuels since the industrial revolution is the main cause of the continuously increasing accumulation of carbon dioxide (CO₂) in the atmosphere, this involves many problems, such as global warming (H. D. Matthews et al., Environ. Res. Lett., vol. 13, p. 10201 (2018)).

One of the most logical solutions is to turn carbon dioxide into an added value product such as fuel or fine chemical, using renewable energy. This could help to decrease industrial CO₂ emission (C. Steinlechner and H. Junge, Angew. Chemie Int. Ed., vol. 57, pp. 44–45, (2018)).

Here we present a theoretical study about a possible new mechanism to produce methanol (CH₃OH) and methane (CH₄) through the hydrogenation of carbon dioxide (CO₂) at standard conditions (Fig. 1). The calculations have been carried out using the G3MP2B3, G4, and W1BD composite methods, and the CCSD method. The results of the study of this uncatalyzed CO₂ hydrogenation will be the primary standard for the evaluation of the catalytic effect of such catalyzed reaction.



124. PYROLYSIS OF SILANES AND SILANE MIXTURES - KINETIC MODELLING AND EXPERIMENTS USING A BENCHTOP REACTOR.

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Abstract

Silane pyrolysis is an important reaction in production of silicon and silicon containing compounds. Silicon is widely used in solar cells and in semiconductor industry. Another application of these materials is in batteries. For example, silicon nitride is used as anode material in Li ion batteries. Studying the reactions in silicon pyrolysis is useful in understanding the production process of silicon, silicon nitride or similar materials.

Pyrolysis of silanes progress through a series of higher order silanes before particle production. The structure and size of these higher order silanes can change with temperature, pressure and other reaction conditions. The characteristics of the higher order silanes influences the particle produced. When silicon nitride is used as an anode material of batteries, the silicon content, size, shape, roughness of particle, etc. influence its electrical properties. Modelling the kinetic scheme of silane pyrolysis is one way to understand the production of higher order silanes.

Theoretical studies focusing on the Si particle formation and Si nucleation are numerous. This study is focusing on the reactions in gaseous phase. A group additivity scheme proposed by Adamczyk et al.¹ is used to calculate the Arrhenius rate parameters E_a (activation energy) and A (pre-exponential factor). A kinetic scheme to understand the process is developed using these parameters.

Silane pyrolysis experiments are done in parallel to validate the kinetic scheme. The reactions are done in a simple bench-top free space reactor and the products are analysed in GC-MS². Previously reported experimental studies in silane pyrolysis are few. The lack of experimental data lead us to calculating some physical parameters. With the main goal of aiding experiments, retention indexes are related to boiling point. The boiling points are extrapolated using Weiner method³.

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125. mHEAT: A PRAGMATIC APPROACH TO SUB-CHEMICAL ACCURACY

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Abstract

Accurate theoretical evaluation of chemical reactions is ultimately limited by the quality of the potential energy surface describing them. Relative energies must be within ± 1 kcal/mol in order to be of 'chemical accuracy', a goal readily achievable with the myriad of composite methods available today. However, recipes that provide sub-chemical accuracy for absolute errors of thermochemical properties while still maintaining a balance between accuracy and efficiency are few and far between. Here we report on our solution to this problem: the modified high accuracy extrapolated *ab initio* thermochemistry protocol, mHEAT.

The mHEAT protocol was born out of the HEAT345-(Q) model chemistry [1]. While 'full' HEAT is capable of sub-kJ errors, the time required precludes its application to molecules with more than a few heavy atoms. The original model chemistry includes three calculations of particular expense: all-electron CCSD(T)/aug-cc-pCV5Z used in the CBS extrapolation, dropped-core CCSDT/cc-pVQZ used in a higher-level correlation extrapolation, and all-electron CCSD(T)/cc-pVQZ force fields used in anharmonic corrections to the ZPE energy.

To reduce the computational cost, these calculations were altered in the following ways. The all-electron, augmented basis set has been replaced by a frozen-core, cc-pVXZ (X=3,4,5) extrapolation. The correlation energy of the core electrons is then recovered via the energy difference between CCSD(T)/cc-pCVQZ when the core is included vs dropped. The high-level CCSDT/cc-pVQZ calculation and corresponding extrapolation are dropped entirely. We believe the simple energy difference between CCSDT and CCSD(T) with the cc-pVTZ basis set is adequate to approximately capture the influence of triple excitations. Last, the all-electron force field calculations using CCSD(T)/cc-pVQZ have been replaced with a hybrid scheme, where the harmonic contributions to the ZPE are calculated using CCSD(T)/ANO1 and the anharmonic terms are calculated via CCSD(T)/ANO0, both within the frozen-core approximation.

These simplifications, along with other relatively minor changes, allow mHEAT to be performed in significantly less time than HEAT345-(Q). We have applied mHEAT to molecules of interest that would be otherwise inaccessible to our study, such as the phenyl radical (C₅H₆) and methyl acetate (CH₃C(O)OCH₃), to good success.

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126. A STUDY OF CHLOROBENZENE PYROLYSIS

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Abstract

The pyrolysis of chlorobenzene under dilute atmosphere and quasi-atmospheric pressure was studied at temperatures from 800 to 1150 K using a fused silica jet stirred reactor (JSR) and from 800 to 1250 K in an alumina tubular reactor. Chlorobenzene was chosen as a surrogate to model the thermal decomposition of polychlorinated biphenyls (PCBs).

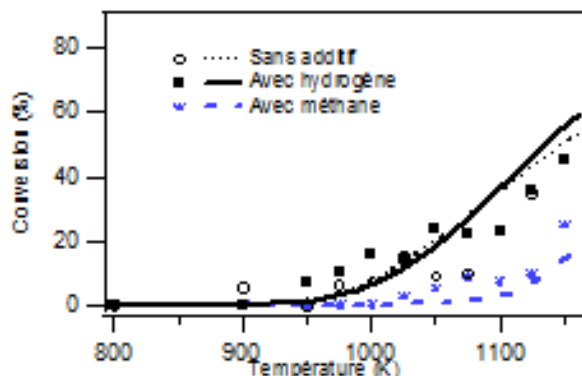
In jet stirred reactor, a maximum chlorobenzene conversion of 48.5 % was observed at a residence time of 2 s, a temperature of 1150 K and an inlet mole fraction of chlorobenzene of 0.005. The following species were quantified: benzene (the major product), HCl (by FTIR measurements), methane, ethylene, acetylene, biphenyl, 1-, 2- and 3-chlorobiphenyl, biphenylene and six isomers of dichlorobiphenyls.

In tubular reactor, a maximum chlorobenzene conversion of 95 % was observed at a temperature of 1250 K under the same conditions as in the jet stirred reactor. The same reaction products were detected but with a larger formation of acetylene and methane and a smaller production of chlorinated and bicyclic compounds.

The effect of two H-atom donors, methane and hydrogen, has been investigated in JSR. Hydrogen addition has a strong inhibiting effect on the formation of chlorinated and bicyclic products.

A new detailed kinetic model was developed and gave a good prediction of the global reactivity, the formation of most major products, and the effect of the addition of hydrogen and methane.

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JSR evolution with temperature during the pyrolysis of chlorobenzene with no additive, with addition of hydrogen and with addition of methane. Symbols are experiments and lines simulations.

127. HYDROXYL RADICAL PRODUCTION FROM REACTIONS OF O₂ WITH SIX C₃ – C₅ ACYL RADICALS

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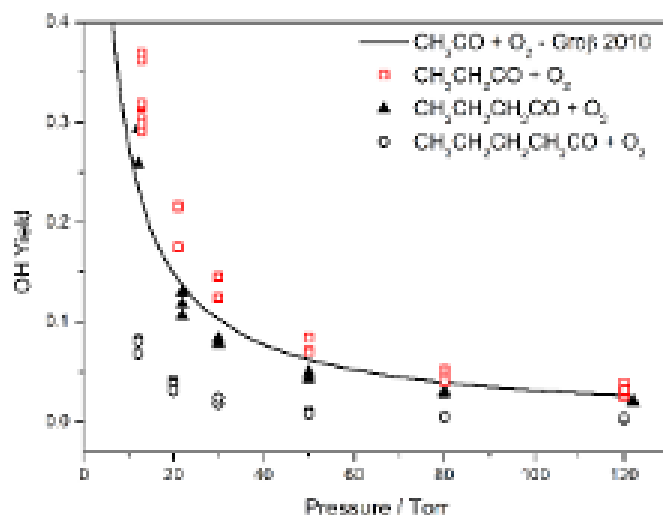
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Abstract

Oxidation of volatile organic compounds (VOC) at low to moderate temperatures characteristic of “cool flames” such as the atmosphere and biofuel engines produces organic peroxy radicals, RO₂. These RO₂ are key intermediates; RO₂ chemistry controls radical termination and of chain-branching processes, notably the regeneration of the primary oxidant hydroxyl radical, OH (1–3).

A new apparatus at the University of York coupled pulsed laser photolysis (PLP) radical generation with pulsed laser induced fluorescence (LIF), for OH detection. All reactions of acyl radicals (RCO) with O₂ produced OH; yields decreased with increasing pressure (Figure 1) in line with previous studies of CH₃CO + O₂ (4). These results are presented in the context of literature data (available only for C₃), and effects of both chain length and chain branching discussed.



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