GK 2012

22ND INTERNATIONAL SYMPOSIUM ON GAS KINETICS

BOULDER

COLORADO • JUNE 18-22

GK2012 SPONSORS

NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION
NOAA
U.S. DEPARTMENT OF COMMERCE

CIRES

NCAR
NATIONAL CENTER FOR ATMOSPHERIC RESEARCH

NSF

RSC | Advancing the Chemical Sciences

Aerodyne Research

Honeywell

Princeton Instruments

Program at a Glance

Sunday (17)		Monday (18)	Tuesday (19)	Wednesday (20)	Thursday (21)	Friday (22)
	6:00 - 7:30	-	Nature Hike	-	Nature Hike	-
	8:50 - 9:00	**Welcome/Logistics**	*Announcements*	*Announcements*	*Announcements*	*Announcements*
	9:00 - 9:20	**Sidney Benson Tribute**	**Multi-phase Chemistry**	**Fundamentals of Chem. Reactivity**	**Alt. Fuels and Renewable Energy**	**Heterogeneous Chemical Processes**
	9:20 - 9:40	**Keynote Address**	**Prof. Hartmut Herrmann**	**Prof. Rex T. Skodje**	**Dr. Timothy J. Wallington**	**Prof. Paul J. Ziemann**
	9:40 - 10:00	**Prof. Michael Pilling**	Ms. Kerry King	Ms. Caroline C. Womack	Prof. G. Barney Ellison	Prof. Yinon Rudich
	10:00 - 10:20	**Multi-phase Chemistry**	Prof. Veronica Vaida	Prof. John R. Barker	Dr. Oliver Welz	Prof. George Marston
	10:20 - 10:40	**Prof. Barbara Finlayson-Pitts**	Dr. John Crowley	Dr. Raghu Sivaramakrishnan	Mr. Shamel S. Merchant	Mr. Benjamin J. Dennis-Smither
	10:40 - 11:10	**BREAK (30 min)**	**BREAK (30 min)**	**BREAK (30 min)**	**BREAK (30 min)**	**BREAK (30 min)**
	11:10 - 11:30	Prof. Markus Ammann	**Exp. Methods and Applications**	**Fundamentals of Chem. Reactivity**	**Alt. Fuels and Renewable Energy**	**Ions and Chemical Processes**
	11:30 - 11:50	Dr. James M. Roberts	**Prof. Markus Kalberer**	**Prof. Kopin Liu**	**Prof. Anthony M. Dean**	**Prof. Veronica M. Bierbaum**
	11:50 - 12:10	Prof. Hans Osthoff	Prof. Lei Zhu	Dr. Sébastien D. Le Picard	Dr. Sebastian Peukert	Prof. Karl-Michael Weitzel
	12:10 - 12:30	Prof. Jesse H. Kroll	Dr. Julien Daranlot	Prof. Amitabha Sinha	Prof. Mathias Olzmann	Dr. Ghanshyam L. Vaghjiani
	12:30 - 12:50	LUNCH	Mr. Eric Osecky	LUNCH	LUNCH	Dr. Ludovic Biennier
	12:50 - 2:00	at C4C	Box Lunch (everyone)	at C4C	at C4C	LUNCH
						at C4C
	2:00 - 2:20	**Combustion Chemistry**	**Excursions**	Prof. Fabien Goulay	**Atmospheric Chemistry**	**ADJORN**
	2:20 - 2:40	**Dr. Craig Taatjes**	**Buses depart ~1 p.m.**	Dr. Albert Wagner	**Dr. Geoffrey S. Tyndall**	
	2:40 - 3:00	Prof. Paul Marshall	**and return ~5 p.m.**	Dr. Josep M. Anglada	Prof. Neil M. Donahue	**Lab Tours: 2:30-5**
	3:00 - 3:20	Dr. Judit Zádor		**Prof. Geoffrey D. Smith**	Prof. John Plane	**CU Chemistry/JILA**
	3:20 - 3:40	Prof. Lev Krasnoperov		**Prof. Renyi Zhang**	Prof. Paul H. Wine	**NCAR**
	3:40 - 4:10	**BREAK (30 min)**		**Prof. Carl J. Percival (3:40-4:00)**	**BREAK (30 min)**	**NOAA (Labs and Science on a Sphere)**
	4:10 - 4:30	Prof. William H. Green		**Prof. Kimberly Prather (4:00-4:20)**	Dr. James Lockhart	
	4:30 - 4:50	Dr. Adam J. Trevitt		-	Prof. Christa Fittschen	
	4:50 - 5:10	Dr. Jeffrey A. Manion		-	Prof. Anthony J. Hynes	
Sign-in and Reception	5:10 - 5:30	Dr. Robert S. Tranter		-	Dr. Bernard Aumont	
5:00-9:00 p.m.	5:30 - 6:30			**Polanyi Lecture: Prof. Mario J. Molina**		
Millenium Hotel		***FREE Evening***	**Poster Session**	*Buses depart: after lecture*	**Poster Session**	
			Stadium Club	**Symposium Banquet**	**Stadium Club**	
			7:00 - 10:00 p.m.	7:00 - 10:00 p.m.	**7:00 - 10:00 p.m.**	

Sidney Benson Lecture

Gas Kinetics - the interface between experiment, theory and application

M J Pilling
School of Chemistry, University of Leeds, Leeds, LS2 9JT, UK

The Sidney Benson lecture is intended as a keynote introductory lecture of the symposium, providing an opportunity to review overall developments in the field and to provide insight to future directions and outstanding major challenges.

Recent years have seen remarkable advances in experimental and theoretical chemical kinetics, which have led and, in some cases been initiated by, applications in a range of areas, especially in the chemistries of combustion, of the atmospheres of the earth and of other planets and of the interstellar medium. Applications place strict requirements of temperature, pressure and concentration on kinetics. Demanding extrapolations are often needed that are increasingly met by a close integration of experiment and theory.

This lecture will touch on a number of topics which illustrate the interface between experiment, theory and applications, many of which are covered in depth in the symposium. These topics include:

- Low temperature combustion of organic compounds and low NO_x atmospheric oxidation of isoprene – reactions of peroxy and hydroperoxy radicals.
- Kinetics at low temperatures – surprises and predictions.
- The role of direct and indirect measurements in the determination of rate coefficients and their uncertainties.
- Reactions in solution – applying ideas from the gas phase.
- Thermodynamic databases.
- Constructing chemical mechanisms.

From the Gas Phase to Particles and Back Again

M. L. Dawson,[1] M. Varner,[1] V. Perraud,[1] M. J. Ezell,[1] L. M. Wingen,[1] R. B. Gerber[1,2] and B. J. Finlayson-Pitts,[1]

[1]University of California, Irvine, CA
[2]Hebrew University of Jerusalem, Jerusalem, Israel.

Airborne particles have well-known effects on health, visibility and climate. A significant fraction of the particle mass and number concentration often arises from gas phase oxidations of organic precursors to form low- and semi-volatile compounds that form new particles or are taken up to grow existing particles to larger sizes. However, major uncertainties exist in understanding how this secondary organic aerosol (SOA) is formed and grows. We report here laboratory studies of new particle formation and growth in some common atmospheric systems, including reactions of methanesulfonic acid as well as the oxidation of several biogenic organic compounds. The key role of experimental and theoretical gas phase kinetics in these systems will be highlighted.

Constraining kinetic parameters of gas particle interactions in the transition from liquid to solid

Markus Ammann[1,*], Sarah Steimer[1], Ming-Tao Lee[1], Goran Grzinic[1], Manabu Shiraiwa[2], Ulrich Pöschl[2], Andrew J. Huisman[3], Ulrich K. Krieger[3], Thomas Peter[3], Thomas Berkemeier[4], and Thomas Koop[4]

[1] Paul Scherrer Institut, Villigen, Switzerland
[2] Max Planck Institute for Chemistry, Mainz, Germany
[3] Institute for Atmospheric and Climate Sciences, ETH, Zürich, Switzerland
[4] Bielefeld University, Bielefeld, Germany
* Corresponding author: Markus.Ammann@psi.ch

Reactive uptake experiments provide a means to understand aerosol aging in the atmosphere. Kinetic limitations in gas particle interactions are not only playing a role in trace gas budgets and particle processing by oxidants, but also in aerosol formation and growth. The recognition of temperature and humidity mediated viscosity changes for organic solutes and their potential effects on chemical and physical processes governing aerosol evolution also in the troposphere have led to a revived interest in better understanding the mechanisms and kinetics of gas-particle interactions (1,2). We have performed uptake experiments of O_3 and nitrogen oxides to a number of aqueous organic and inorganic or mixed composition substrates to constrain the kinetics of these systems under a wider range of physical conditions, i.e., solid, semi-solid, and liquid, by means of surface accommodation, surface reactions, surface to bulk transfer, bulk diffusion and reaction (3-5). Previous and new data are reanalyzed by fitting with a kinetic flux model (6) that allows to explicitly track non-steady state conditions especially within the particle bulk to account for diffusion of the reactants. Some of the issues related to constrain kinetic parameters and to differentiate surface from bulk processes based on datasets typically limited in coverage of parameter space are discussed.

References

(1) Koop, T.; Bookhold, J.; Shiraiwa, M.; Pöschl, U. *Phys. Chem. Chem. Phys.*, **2011**, 13,
(2) Shiraiwa, M.; Ammann, M.; Koop, T.; Pöschl, U. *Proc. Natl. Acad. Sci.* **2012**, 108, 11003-11008.
(3) Rouvière, A.; Sosedova, Y.; Ammann, M. *J. Phys. Chem. A*, **2010**, 114, 7085-7093.
(4) Sosedova, Y.; Rouvière, A.; Gäggeler, H. W. Ammann, M. *J. Phys. Chem. A*, **2009**, 113, 10979-10987.
(5) Sosedova Y.; Rouviere A.; Bartels-Rausch T.; Ammann M. *Photochem. Photobiol. Sci.*, 2011.
(6) Shiraiwa, M.; Pfrang, C.; Poeschl, U. *Atmos. Chem. Phys.*, **2010**, 10, 3673-3691. 19238-19255.

The Multi-phase Atmospheric Chemistry of Isocyanic Acid, HNCO

James M. Roberts,[1*] Patrick R. Veres,[2, 3] Anthony K. Cochran[4], Trevor VandenBoer[5], Carsten Warneke[2], Martin Graus[2], Joost de Gouw[2], Ann M. Middlebrook[1], Roya Bahreini[2], Fatma Ozturk[2], Charles A. Brock[1], Ian R. Burling[6], and Robert J. Yokelson[6]

[1] National Oceanic and Atmospheric Administration (NOAA), Boulder, CO, USA
[2] Cooperative Institute for Research in the Environmental Sciences, University of Colorado, Boulder, CO, USA
[3] now at Max Planck Institute for Chemistry, Mainz, Germany
[4] North Carolina A&T University, Greensboro, NC, USA
[5] Department of Chemistry, University of Toronto, Toronto, Canada
[6] Department of Chemistry, University of Montana, Missoula, MT, USA
* Corresponding author: James.M.Roberts@noaa.gov

Isocyanic acid is a common and relatively abundant product of combustion of nitrogen-containing fuels, especially biomass. There also appear to be sources of HNCO in the atmosphere from photooxidation of reduced nitrogen species, e.g. amines. Removal of HNCO from the atmosphere by reaction with OH, or other radicals, is very slow (years), and photolysis is less certain but also likely to be slow (months). As a result, wet and dry deposition are the processes controlling atmospheric removal of HNCO. As a weak acid (pKa = 3.7), HNCO exhibits pH-dependent solubility in aqueous solution, and is quite soluble ($H>10^5$ M/atm) at physiologic pH (7.4) (e.g. in the human lung). Recent biochemical studies have shown that known smoke-related health effects can be linked to protein carbamylation driven by cyanate ion at solution concentrations (100μM), equivalent to 1 ppbv HNCO in the gas phase. Measurement of HNCO in ambient air by negative ion proton-transfer chemical ionization mass spectrometry has shown that HNCO can often approach or exceed 1 ppbv in plumes from wild or agricultural fires, making it important that we understand potential exposure to this possible health hazard. This presentation will focus on the multi-phase behavior of HNCO and some assessments will be made of the effect of hydrolysis on HNCO atmospheric lifetimes and the importance of aerosol-phase reactions to form carbamylated products.

References

(1) Roberts, J. M.; Veres, P. R.; Cochran, A. K.; Warneke, C.; Burling, I. R.; Yokelson, R. J.; Lerner, B. M.; Gilman, J. B.; Kuster, W. C.; Fall, R.; de Gouw, J., *PNAS,* **2011,** *108*, 8966-8971.

Multi-phase Chemical Processes
Oral Monday 11:50 – 12:10

Production of gas-phase nitrogen dioxide and nitrous, peroxynitrous and peroxynitric acid from photolysis of nitrate in ice

Otman Abida[1,2] and Hans D. Osthoff [1,*]

[1] University of Calgary, Calgary, AB, Canada
[2] Now at: State University of New York, Albany, NY, USA
* Corresponding author: hosthoff@ucalgary.ca

Photochemically induced emissions from the surfaces of snow and ice crystals are known to alter the composition of the troposphere. In particular, photolysis of the nitrate anion (NO_3^-) in snow and ice has been shown to yield NO_x (= $NO+NO_2$) and nitrous acid (HONO) in the gas-phase. Subsequent photolysis reactions involving HONO and NO_x can alter the oxidative balance of the atmosphere and increase the rate of formation of the greenhouse gas ozone, significantly affecting the composition of the polar boundary layer.

In this work, we examined the nitrogen oxides evolved from irradiated frozen solutions containing nitrate as a function of acidity[1,2] and in the presence of selected organic compounds.[3] Gas-phase products were monitored by cavity ring-down spectroscopy, NO-O_3 chemiluminescence, and chemical ionization mass spectrometry. The photochemical release of NO_2 from irradiated frozen solutions containing NO_3^- was promoted by acidic conditions similar to those found in moderately polluted environments. In unbuffered ice or under basic conditions, the main gas-phase nitrogen oxide observed was NO_2 (>95% relative to odd nitrogen, or NO_y). The yield of gas-phase NO_2 increased with decreasing pH (measured prior to freezing) in the range from 9.5 to 4.5. Acid-promoted production of NO_2 is rationalized by formation of peroxynitrous (HOONO), which was observed alongside peroxynitric acid (HO_2NO_2) in the gas-phase. Under very acidic conditions ($pH < 4.5$), production of additional nitrogen oxides was in the form of species belonging to NO_z, i.e., nitrous (HONO) and nitric acid ($HONO_2$). The presence of formate, methanesulfonate, toluene or phenol suppressed production of gas-phase nitrogen oxides. In contrast, para-halogenated phenols (in the order of Cl>Br>F) promoted the conversion of NO_3^- to gas-phase nitrogen oxides, rationalized by acidification of the ice surface. Acid-promoted conversion of condensed-phase NO_3^- to gas-phase NO_2 is currently not considered in atmospheric chemistry and aerosol models but may be a significant but overlooked aerosol nitrate volatilization pathway and source of OH radicals in the troposphere.

References

(1) Abida, O.; Mielke, L.H.; Osthoff, H.D. *Chem. Phys. Lett.* **2011**, 511, 187-192.
(2) Abida, O.; Osthoff, H.D. *Geophys. Res. Lett.* **2011**, 38, L16808.
(3) Abida, O.; Osthoff, H.D. *J. Phys. Chem. A* **2012**, article ASAP, doi: 10.1021/jp210249t.

Kinetics of the multiphase formation of oxidized organic aerosol

Jesse H. Kroll,[1,2*] Kelly E. Daumit,[1] James F. Hunter,[1] Sean H. Kessler,[1] and Kevin R. Wilson[2]

[1] Massachusetts Institute of Technology, Cambridge, MA, USA
[2] Lawrence Berkeley National Laboratory, Berkeley, CA, USA
* Corresponding author: jhkroll@mit.edu

Atmospheric organic aerosol (OA) tends to be substantially higher in mass loading and carbon oxidation state than OA produced in laboratory studies, suggesting major gaps in our understanding of the chemistry underlying OA formation and/or evolution. In recent years a number of pathways have been put forth as possible mechanisms for the generation of large amounts of highly oxidized OA. However, assessing the viability of these schemes as key atmospheric OA sources is difficult, in part because their kinetics tend to be poorly constrained. This prevents comparisons between laboratory data and ambient observations, namely the observed formation timescales of oxidized OA (on the order of one day in the atmosphere). Here we present a series of laboratory studies of the formation of oxidized organic aerosol, focusing not only on the reaction products (as described by the abundance and average oxidation state of particulate organic carbon), but also on the rate at which these products are formed. Oxidative "aging" of secondary organic aerosol mixtures (in which gas-phase reaction products are exposed to sustained concentrations of hydroxyl radicals) is found to lead to increases in both particle mass and degree of oxidation, but over timescales substantially longer than a day. Heterogeneous oxidation of particulate organics is similarly found to be too slow to account for observations of oxidized OA formation, consistent with results from a number of other studies. Multiphase chemistry – the oxidation of species within liquid (organic or aqueous) droplets – has been suggested as an alternative mechanism for the efficient formation of highly oxidized OA. However this process can also be quite slow under atmospheric conditions, because the organics must first partition into the condensed phase prior to being oxidized. Therefore both oxidation and gas-particle partitioning govern the kinetics of these reactions; consideration of both together may suggest important channels for the rapid formation of highly oxidized, low-volatility organics.

Measuring reactions of key intermediates in hydrocarbon oxidation

Craig A. Taatjes

Combustion Research Facility, Sandia National Laboratories, MS 9055, Livermore, CA 94551-0969, USA

The oxidation of hydrocarbons in combustion or other systems involves a complicated web of chemical transformations, passing through multiple unstable intermediates. Modeling the oxidation process requires understanding how these intermediates react. However it is unsettlingly common that critical intermediate species cannot be readily interrogated, and that the kinetics of key reactions must be inferred from indirect measurements. I will discuss recent combinations of experiment and theory that indirectly reach inside the "black box" of oxidation processes to probe the underlying mechanisms of important reactions, with particular emphasis on understanding the fundamental chemistry relevant to autoignition of traditional, non-traditional, and alternative fuels. Moreover I will highlight recent progress towards *direct* measurement of the kinetics of some elusive intermediates in combustion and tropospheric chemistry.

This work is supported by the Division of Chemical Sciences, Geosciences, and Biosciences, the Office of Basic Energy Sciences, and the U.S. Department of Energy, and by the Laboratory Directed Research and Development (LDRD) program at Sandia National Laboratories. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the National Nuclear Security Administration under contract DE-AC04-94-AL85000.

Kinetic Studies of the Reactions of NH_2 Radicals with H_2S and SO_2: Differing Roles for Bound Intermediates

Yide Gao[1] and Paul Marshall[1,*]

[1] University of North Texas, TX, USA
* Corresponding author: marshall@unt.edu

Amino radicals are key intermediates in the production of nitrogen oxides in combustion. Sulfur in fuels can have an impact on the extent of NOx formation, and the reactions

$$NH_2 + SO_2\ (+\ M) \rightarrow \text{products}\ (+\ M) \qquad (1)$$

$$NH_2 + H_2S\ (+\ M) \rightarrow \text{products}\ (+\ M) \qquad (2)$$

have been investigated as part of an effort to establish a mechanism for interactions between sulfur and nitrogen species.

Ground-state NH_2 was generated by pulsed photolysis of NH_3 precursor at 193 nm, and monitored by time-resolved laser-induced fluorescence at 570.3 nm, in the presence of excess molecular reactant in an Ar bath gas. For reaction 1, experiments were conducted over 298 – 550 K and at pressures from 9 to 25 mbar, and pressure-dependent kinetics were observed close to the low-pressure limit, with $k_0 \approx 1.2 \times 10^{-31}$ cm^6 molecule^{-2} s^{-1} which did not vary significantly with temperature. This contrasts with a prior study where fall-off was observed at very low pressures (1). The high-pressure limit was estimated from the removal rate constant of vibrationally-excited (0,1,0) NH_2 (detected via LIF at a wavelength of 531.8 nm) as approximately 1.6×10^{-11} cm^3 molecule^{-1} s^{-1}. These results are rationalized in terms of RRKM theory and an NH_2-SO_2 binding energy of about 75 kJ mol^{-1}, which was computed via coupled-cluster theory extrapolated to the complete basis set limit. Possible subsequent chemistry of this adduct is discussed.

Reaction 2 was investigated over 295 – 820 K. The rate constant was observed to be independent of pressure and temperature, with $k_2 \approx 4.3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The removal rate constant for excited NH_2 (0,1,0) is approximately 1.5×10^{-11} cm^3 molecule^{-1} s^{-1}. The potential energy surface indicates a weakly bound adduct between NH_2 and H_2S in the entrance channel, and its influence on the unexpectedly slow kinetics is explored via RRKM theory. The adduct is not stable enough to be a final sink for NH_2 and a modest barrier to formation of NH_3 + SH is characterized by *ab initio* methods. The results are contrasted with the behavior of the analogous OH + H_2S system (2).

References

(1) Ioffe, A.A.; Bulatov, V.P.; Lozovsky, V.A.; Goldenberg, M.Y.; Sarkosov, O.M.; Umansky, S.Y. *Chem. Phys. Lett.* **1989**, 156, 425-432.
(2) Ellingson, B.A.; Truhlar, D.G. *J. Amer. Chem. Soc.* **2007**, 129, 12765-12771.

$^{\bullet}$QOOH decomposition and the $^{\bullet}$QOOH + O_2 reaction: Direct experimental investigation and theory

Judit Zádor,[1,*] Haifeng Huang,[1] Oliver Welz,[1] Johan Zetterberg,[2] David L. Osborn[1] and Craig A. Taatjes[1]

[1] Sandia National Laboratories, Livermore, CA, USA
[2] Lund University, Lund, Sweden
* Corresponding author: jzador@sandia.gov

The carbon-centered hydroperoxyalkyl radicals, often referred to as $^{\bullet}$QOOH, play a central role in the autoignition kinetics of alkanes at low temperatures (<~800 K), because they participate in important chain propagating and chain branching reactions. The formation of these radicals in the gas-phase by internal H-abstraction from the corresponding peroxyalkyl radicals (ROO$^{\bullet}$) was postulated at least as early as 1965[1] based on product studies. With the advancement of computational and theoretical chemistry the pathways leading to these highly unstable radicals have been established.[2,3] $^{\bullet}$QOOHs are ubiquitous in every complex chemical model describing low-temperature autoignition of alkanes or related compounds, yet, these ephemeral species have never been observed directly, nor have their kinetics been studied in isolation.

In this work we present the first direct measurements on the kinetics of a $^{\bullet}$QOOH radical. The *tert*-butyl hydroperoxy radicals are generated from *tert*-butylhydroperoxide by abstracting one of the nine methyl hydrogens by a photolytically generated Cl-atom. The fate of this $^{\bullet}$QOOH radical and its reaction with molecular oxygen was monitored in two low-pressure experimental setups at room temperature. In one experiment we probed the OH radicals, which are direct products from the thermal decomposition of this $^{\bullet}$QOOH radical, in a reaction flow cell by multi-pass direct absorption at 2.87 μm wavelength to obtain time-resolved absolute OH concentrations. We additionally performed multiplexed synchrotron photoionization mass spectrometry (MPIMS) experiments at the Chemical Dynamics Beamline at the Advanced Light Source to obtain mass-, isomer- and time-resolved profiles of the chemical species involved, providing further, complementary insight into the chemical mechanism. Finally, the chemical system was described using high-level theoretical calculations, employing *ab initio* transition-state master-equation methods as well as a small chemical model to account for the secondary chemistry in the experiments.

Our combined experimental and theoretical effort enabled us to make the first direct investigation of a $^{\bullet}$QOOH species: we measured rate coefficients and branching fractions of its decomposition reaction and of its reaction with O_2. This information, in turn, can be used to constrain both our theoretical approaches and larger chemical models.

References

(1) Benson, S.W. *J. Am. Chem. Soc.* **1965**, 87, 927-979.
(2) Miller, J.A.; Klippenstein, S.J.; Robertson, S.H. *Proc. Comb. Inst.* **2000**, 28, 1479-1486.
(3) Zádor, J.; Fernandes, R.X.; Taatjes, C.A. *Prog. Energy Comb. Sci.* **2011**, 37, 371-421.

Kinetics of Reactions of Combustion Importance at Elevated Temperatures and Pressures

Manuvesh Sangwan,[1] Evgeny N. Chesnokov,[2] and Lev N. Krasnoperov[1,*]

[1] New Jersey Institute of Technology, Newark, NJ, USA
[2] Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia
* Corresponding author: krasnoperov@adm.njit.edu

An experimental study of several elementary reactions of methyl and hydroxyl radicals over extended (0.01 - 100 bar, 298 – 834 K for OH+OH, 1-100 bar, 298 – 715 K for CH_3+OH and CH_3+CH_3) pressure and temperature ranges by pulsed excimer laser photolysis coupled with transient absorption spectroscopy was completed. Acetone was used as a photochemical precursor of CH_3 radicals at 193 nm, photolysis of N_2O/H_2O was used to produce OH radicals at 193 nm (via the fast reaction $O(^1D) + H_2O$). Methyl and hydroxyl radicals were monitored by transient absorption at 215 nm and 308 nm, respectively.

In the reaction of methyl radicals with hydroxyl radicals

$$\begin{array}{lllllll} CH_3 & + & OH & \rightarrow & {}^1CH_2 & + & H_2O \quad (1a) \\ & & & \rightarrow & CH_3OH & & \quad (1b) \\ & & & \rightarrow & \text{other products} & & \quad (1c) \end{array}$$

no pressure dependence was found over the pressure range 1 – 100 bar at all temperatures, indicating negligible contribution of the pressure dependent stabilization channel 1b. These measurements fill the gap between the near ambient temperature and high temperature shock tube studies of reaction 1.[1,2]

In the self-reaction of hydroxyl radical

$$\begin{array}{lllllll} OH & + & OH & \rightarrow & H_2O & + & O \quad (2a) \\ & & & \rightarrow & H_2O_2 & & \quad (2b) \end{array}$$

new parameterization of the pressure dependent channel 2b was obtained (Fig. 1). The low pressure extrapolation of the high temperature data combined with the literature data and our recent measurements at low temperatures unambiguously indicate a turning point in the temperature dependence of the rate constant of reaction 2a at about 500 K.

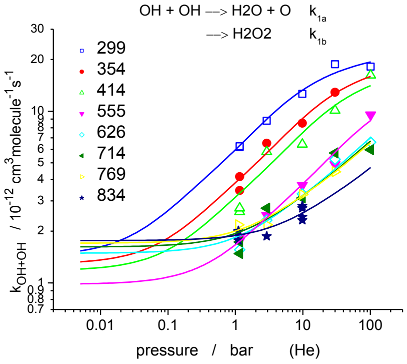


Figure 1.

The rate constant of recombination of methyl radicals 3 was characterized over the extended temperature and pressure ranges.

$$CH_3 \quad + \quad CH_3 \quad \rightarrow \quad C_2H_6 \qquad (3)$$

References

(1) Krasnoperov, L. N.; Michael, J. V. *J. Phys. Chem. A.* **2004**, 108, 8317-8323.
(2) Vasudevan, V.; Cook, R. D.; Hanson, R. K.; Bowman, C. T.; Golden D. M. *Int. J. Chem. Kin.* **2008**, 40, 488-495.

Automated Predictive Chemical Kinetics: Triumphs and Challenges

William H. Green[1,*], Jorge Aguilera-Iparraguirre[1], Ionut M. Alecu[1], Joshua W. Allen[1], Caleb A. Class[1], Connie W. Gao[1], Amrit Jalan[1], Gregory R. Magoon[1], Shamel Merchant[1], Nick Vandewiele[2], Kevin M. Van Geem[2], Richard H. West[3], Everton Fernando Zanoelo[4]

[1] Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA
[2] Laboratory for Chemical Technology, University of Ghent, Belgium
[3] Department of Chemical Engineering, Northeastern University, Boston, MA, USA
[4] Department of Chemical Engineering, Universidade Federal do Parana, Curitiba, PR, Brazil
* Corresponding author: whgreen@mit.edu

A long-term goal of the chemical kinetics community is to be able to quantitatively predict the time evolution of a reacting mixture. The ability to do this quickly and reliably would completely transform many areas of technology which currently rely on rough estimates and trial-and-error experimentation. To be fast/efficient enough to be practically useful, the whole process of making the predictions needs to be automated.

Advances in rate theory, quantum chemistry, and kinetic modeling algorithms, coupled with the constantly increasing number of accurate experimental rate coefficients and thermochemical parameters, are beginning to make it possible to quantitatively predict chemical kinetics even in the absence of experiments in some cases. However, these predictions are not yet reliably accurate, so experimental validation is highly advisable. Some of the triumphs and failures of predictive chemical kinetics using the open-source RMG software are highlighted, using as examples the combustion of butanol isomers, the pyrolysis of the synthetic jet fuel JP-10, and reactions of organic sulfides in supercritical water. The reasons for the failures are examined. We outline several challenges that the kinetics community must overcome before we will achieve our long-term goal of reliable quantitative predictions for reacting mixtures.

Synchrotron Product Detection Studies of Ortho and Meta Methylphenyl + O_2

Adam J. Trevitt,[1*] John D. Savee,[2] David L. Osborn,[2] Craig. A. Taatjes[2] and Gabriel da Silva[3]

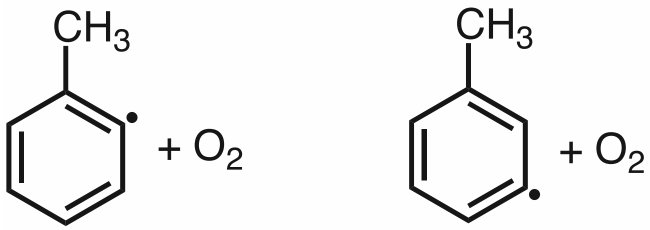
[1] University of Wollongong, NSW, Australia
[2] Combustion Research Facility, Sandia National Laboratories, CA, USA
[3] University of Melbourne, Vic, Australia
* Corresponding author: adamt@uow.edu.au

Conventional combustion chemistry is predominantly driven by reactions of hydrocarbon radicals with O_2. In the case of the aromatic-fuel archetype toluene ($C_6H_5CH_3$), its corresponding radical benzyl ($C_6H_5CH_2$) is relatively resilient to molecular oxygen and this underpins toluene's resistance to autoignition. It is emerging however, that the reactive methylphenyl ($C_6H_4CH_3$) isomers of benzyl, formed in low levels through the initial attack of OH on toluene, warrant consideration. Recent kinetic modeling of toluene oxidation in a flow reactor finds that the methylphenyl channel accounts for 15% of the initial destruction of toluene.[1] To date there have been few experimental studies of these methylphenyl oxidation reactions. To address this, we utilize synchrotron photoionisation mass spectrometry (PIMS) performed at the Chemical Dynamics Beamline of the Advanced Light Source (Berkeley, USA) to examine the products of the *ortho*-methylphenyl + O_2 reaction. Comparisons are made to the *meta*-methylphenyl + O_2. These reactions are first studied at room temperature and 4 Torr.

Oxidation products are detected on several mass channels for both the *ortho* and *meta*-methylphenyl isomers; the *ortho* case contains two additional significant products. In both cases, O-atom loss is a major product channel. For *o*-methylphenyl + O_2, the presence of the methyl group at the *ortho* position provides additional pathways for the peroxyl radical intermediate to rearrange. Ultimately, this leads to two unique product channels, corresponding to OH elimination and CH_3CO elimination. For both reactions we discuss the likely chemical pathways to these products drawing on computationally derived potential energy diagrams. This enables us to explain some of the underlying chemistry leading to the observed products.

References

(1) Metcalfe, W. K.; Dooley, S.; Dryer, F. L. *Energy Fuels* **2011**, *25*, 4915.



Pressure Dependence of the Decomposition of *n*-Pentyl Radicals near 1000 K

Jeffrey A. Manion,[1,*] Andrea Comandini,[2] Iftikhar A. Awan, [1] and
Donald R. Burgess, Jr. [1]

[1] National Institute of Standards and Technology, Gaithersburg, Maryland, 20899-8320, USA
[2] University of Illinois, Chicago, IL 60607 USA
* Corresponding author: jeffrey.manion@nist.gov

Alkyl radicals are important intermediates in the combustion of hydrocarbon fuels and an understanding of their behavior is needed over a wide range of pressures and temperatures. The decomposition and intramolecular H-transfer isomerization reactions of the 1-pentyl radical have been studied over an extended pressure range in joint shock tube studies carried out at the National Institute of Standards and Technology (NIST) and the University of Illinois. Experiments were performed in an argon bath gas at temperatures between 850 K and 1070 K and pressures of 80 kPa to 680 kPa (NIST) and 2300 kPa to 5000 kPa (University of Illinois). 1-pentyl radicals are generated by shock heating dilute mixtures of 1-iodopentane and the stable olefin products of its decomposition observed by post-shock gas chromatographic analysis. Ethene and propene are the main olefin products and account for > 97% of the carbon balance from the 1-pentyl radical. The ethene/propene ratio can be can be related to the concentrations of 1-pentyl and 2-pentyl radicals in the system and the relative rates of 5-center intramolecular H-transfer reactions and beta C-C bond scissions. 3-pentyl radicals, formed via four-center intramolecular H transfers, lead to 1-butene and play only a very minor role in the system. Beta C-H bond scissions in the radical intermediates are likewise of minor importance. Ethene/propene product ratios are temperature and pressure dependent and vary from about 3 to 7 over the experimental conditions. The ratio appears to approach high pressure limiting values at the highest pressures studied. A consistent kinetics model that reproduces the observed branching ratios and pressure effects has been developed on the basis of the present experiments, a Rice Ramsberger Kassel Marcus/Master Equation (RRKM/ME) analysis, computational chemistry results, and relevant experimental literature data from lower temperatures. If an exponential-down model is employed for energy transfer, the results require a value of $<\Delta E_{\mathrm{down}}(1000\ \mathrm{K})> = (675 \pm 100)\ \mathrm{cm}^{-1}$ for the average energy transferred in deactivating collisions in an argon bath gas. The present model can be used to extrapolate the results over a wide range of conditions of interest.

High temperature sources of phenyl and benzyne radicals and their reactions.

Robert S. Tranter[1*], Patrick T. Lynch[1], And Christopher J. Annesley[1]

[1] Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Il, USA.

* Corresponding author: Tranter@anl.gov

Recent results have emphasized the importance of *o*-benzyne radicals (*o*-C_6H_4) [1] along with phenyl radicals (C_6H_5) [2] in aromatic pyrolysis and soot formation. In the varied conditions of combustion systems, these radicals participate in dissociation [3], recombination, and addition reactions [4] and lead to soot formation by a variety of routes. It is therefore important to measure the high temperature reactions of these radicals and determine their pressure dependencies. High temperature thermal dissociation sources of these radicals are limited, and their characterization is also limited. Recently, diiodobenzene [5], dimethylbenzene [6], and phtalic anhydride [4] have been used successfully as sources for *o*-C_6H_4, although the low volatility of diiodobenzene and pthalic anhydride could limit their more general use.

We have used halo-benzenes (C_6H_5X, X=F,Cl,Br,I) as a source of phenyl and *o*-benzyne radicals over a very wide temperature range in a diaphragmless shock tube. We have measured the initial dissociation of these molecules and studied dissociation and recombination reactions of o-benzyne and phenyl radicals by laser schlieren densitometry and time-of-flight mass spectrometry at temperatures between 1275 K and 2900 K. The dissociation mechanisms for the halobezenes vary from predominantly C-X scission in iodo-benzene to almost exclusively H-X elimination from fluorobenzene with C_6H_5Br/Cl exhibiting a mixture of scission and elimination. Secondary reactions between the parent molecules and radical products are also important with the fluoro and chloro benzenes. The use of halobenzens as radical sources will be discussed along with results on the dissociation of *o*-benzyne and recombination of phenyl radicals.

References

(1) Comandini, A.; Brezinsky, K.; *J. Phys. Chem. A*. **2011**, 115, 5547-5559.
(2) Tranter, R. S.; Klippenstein, S. J.; Harding, L. B.; Giri, B. R.; Yang, X.; Kiefer, J. H. *J. Phys. Chem. A* **2010**, 114, 8240.
(3) Wang, H.; Laskin, A.; Moriarty, N.; Frenklach, M.; *Proc. Combust. Inst.* **2000,** 28, 1545-1555.
(4) Friedrichs, G.; Goos, E.; Gripp, J.; Nicken, H.; Schönborn, J.; Vogel, H.; Temps, F.; *Z. Phys. Chem.* **2009**, 223, 387-407.
(5) Xu, C.; Braun-Unkhoff, M.; Naumann, C.; Frank, P.; *Proc. Combust. Inst.*, **2007** 31, 231-239.
(6) Zhang. X.; Maccarone, A.; Nimlos, M.; Kato, S.; Bierbaum, V.; Ellison, G.; Ruscic, B.; Simmonet, A.; Allen, W.; Schaefer, H.; *J. Chem Phys.* **2007**, 126, 044312.

Tropospheric multiphase chemistry in lab, modeling and field studies

Hartmut Herrmann,[1,*] Christian Weller, Thomas Schaefer, Luisa Schöne, Janine Schindelka, Andreas Tilgner, Peter Bräuer, Dominik van Pinxteren, Konrad Müller, Laurent Poulain, Yoshiteru Iinuma, Lisa Whalley[2], Dwayne Heard[2] and Gerald Spindler

[1] Leibniz-Institute for Tropospheric Research, Chemistry Dept., Leipzig, Germany
[2] University of Leeds, School of Chemistry, UK
* Corresponding author: herrmann@tropos.de

In the first part of this contribution an overview on tropospheric multiphase chemistry studies is given with emphasis on laboratory experiments. Aqueous phase kinetics and mechanisms are studied by laser-based methods and examples for the multiphase oxidation of compounds of interest (such as acetone, isoprene) will be given. Recently, investigations on non-radical oxidation reactions were initiated and, in addition, investigations of reactions in organic phase proxies were tested to come to kinetic data of interest for tropospheric organic particle chemistry. Both of these efforts will be described.

In the second part, the interplay with chemical mechanism development will be outlined and some recent results obtained by simulations with the CAPRAM chemical scheme will be presented including results from a joint study to set–up an aqueous phase chemistry mechanism generator.

Finally, in the third part, an effort to investigate aerosol-cloud chemistry in a complex ground based study (HCCT-2010) is described and first results are presented.

A summary and outlook will be given accounting for recent progress and trying to identify our current major gaps of knowledge.

Dynamics of interfacial collisions of OH with organic liquid surfaces

Kerry L. King, [1] Grant Paterson, [1] Matthew L. Costen[1] and Kenneth G. McKendrick[1,*]
[1] Heriot-Watt University, Edinburgh, EH14 4AS.
* Corresponding author: Kenneth.G.McKendrick@hw.ac.uk

The dynamics of potentially reactive gas-liquid interfacial collisions remain relatively unexplored, but are of intrinsic fundamental interest. They are also of widespread applied importance, for example in heterogeneous atmospheric chemistry. We present an experimental investigation of the dynamics of gas-liquid interfacial collisions of OH radicals with organic liquids chosen partly for their interest as mimics of the surfaces of atmospheric aerosols.

The OH radicals were produced by photolysis of a gas-phase precursor. Those that survive and recoil from the continually refreshed liquid surface are intercepted by a tunable probe laser beam which excites laser-induced fluorescence (LIF) on the OH A-X band.

Two different precursors were used to enable a range of translational and internal OH energy distributions to be prepared. More recent measurements used photolysis of allyl alcohol at 193 nm, generating OH that is both translationally ($<E_T> \sim 85$ kJ mol^{-1}) and rotationally ($T_{rot} \sim 2000$ K in both $v = 0$ and 1) excited. This complements previous work based on photolysis of HONO at 355 nm, resulting in translationally hot ($<E_T> \sim 54$ kJ mol^{-1}) but rotationally colder (close to thermal) OH.[1,2] We have characterized the collisions of both these distributions with the surfaces of a series of liquids, including an inert reference, PFPE (perfluoropolyether), and representative long-chain, partially branched saturated and unsaturated hydrocarbons. Two distinct types of measurements have been made. The first is the appearance profile for a particular scattered product level as a function of photolysis-probe delay. This contains information on the internal state-specific translational energy distribution. The second is the LIF excitation spectrum at a fixed delay, revealing the internal product-state distribution for a velocity subgroup. Contributions from molecules that have not collided with the surface are removed by subtraction of the corresponding data with no liquid surface present.

We find strong and unambiguous positive correlations between product rotation and translation in the scattered OH $v' = 0$ products for all the liquids examined. This is particularly clear for the rotationally hotter OH from allyl alcohol. Overall, this OH experiences a significant net rotational cooling. In contrast, for HONO, the dominant scattering process is T→R transfer, with a gain in rotational energy at all the surfaces.[2] There are clear differences in the inelastic scattering from different liquids, with, as expected, PFPE presenting a 'harder' surface than the hydrocarbons. These observations can be interpreted in terms of a combination of direct, ballistic scattering, and indirect thermal desorption. The reactive uptake can also be inferred from comparison of the OH yield from PFPE with that from the other liquids. OH is lost at both saturated and unsaturated hydrocarbon surfaces. A very interesting subtlety is that although the survival probability of the directly scattered OH is similar in both cases, it is distinctly lower for rotationally and translationally cold OH from unsaturated surfaces. This is consistent with an additional reactive loss channel due to capture of thermalised OH at the double-bond sites.

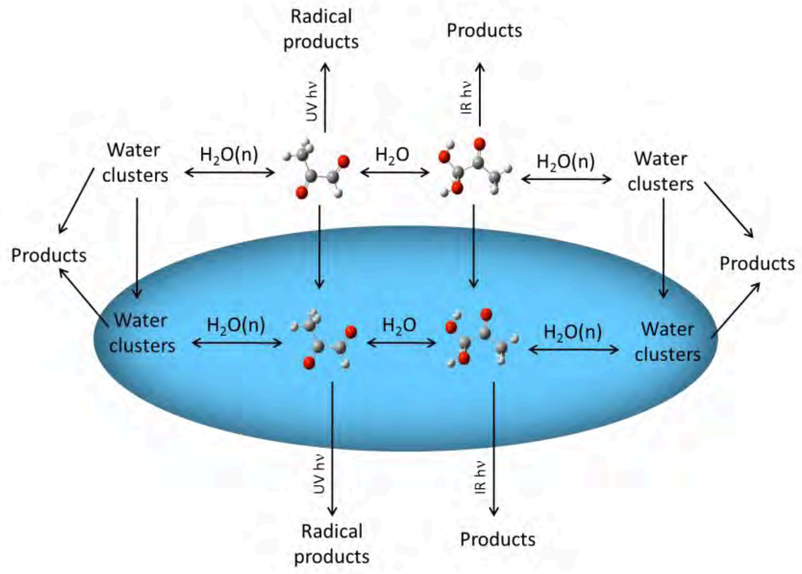
1. P. A. J. Bagot, C. Waring, M. L. Costen and K. G. McKendrick, *J. Phys. Chem. C*, 2008, **112**, 10868-10877.
2. C. Waring, K. L. King, P. A. J. Bagot, M. L. Costen and K. G. McKendrick, *Phys. Chem. Chem. Phys.*, 2011, **13**, 8457-8469.

Atmospheric Consequences of the Hydration in Gas Phase of Aldehydes and Ketones

Veronica Vaida and Jessica L Axson

Department of Chemistry and Biochemistry, Campus Box 215, University of Colorado, Boulder, CO 80309, USA
CIRES, Campus Box 215, University of Colorado, Boulder, CO 80309, USA

Aldehydes and ketones are known oxidation products of biogenic and anthropogenic VOCs and have been observed by field studies to be present in aerosol and cloud particles. While the gas-phase chemistry of these compounds is fairly well understood, their modeled concentration and role in SOA formation remains controversial. In aqueous solution aldehydes and ketones hydrate to form alcohols. We explore the hydration of these compounds in the gas phase and examine the water and photon mediated processes of these hydrates. The formation of hydrates can contribute to aerosol growth and formation by partitioning into clouds and aerosols because of their lower vapor pressure and tendency to form intermolecular hydrogen bonds. Hydration of aldehydes and ketones has important consequences to the atmospheric photochemistry of these organic compounds. The experimental approaches employ Fourier transform spectroscopy (FTS) and cavity ringdown spectroscopy (CRDS) to observe the formation of diols and hydrates by these molecules as a function of relative humidity.



Trace-gas burial in growing ice

Matthias Kippenberger,[1] John Crowley* and Gerhard Schuster

[1] Max-Planck-Institut für Chemie, Mainz, Germany.
* Corresponding author: John.Crowley@mpic.de

Atmospheric ice is rarely in perfect equilibrium with water vapor but is constantly growing or evaporating. Trace gases impinging on growing ice surfaces can be buried in newly formed layers of ice, resulting in repartitioning from the gas to the ice phase and thus impacting on gas- and particle-phase composition and chemistry.

Whilst aircraft observations suggest that trapping takes place in cirrus clouds, there are few quantitative laboratory data describing this effect. We have investigated the trapping of a variety of trace gases on growing ice films with the goal of deepening our understanding of the trapping process and its dependence on environmental variables such as the ice growth rate, temperature and trace gas partial pressure. Data on the uptake of several organic traces gases and HCl were obtained using a low-pressure reactor connected to a chemical-ionisation mass-spectrometer. We present a parameterisation of the burial efficiency and compare this with reversible surface uptake.

Experimental Methods and Applications
Invited Tuesday 11:10 – 11:50

Recent advances in mass spectrometry techniques to determine the composition and reactivity of atmospheric aerosols

Markus Kalberer,[1*] Francis D. Pope,[1,2] Stephen J. Fuller,[1] Peter J. Gallimore,[1] Angela G. Rincon,[1] and Ivan Kourtchev[1]

[1] Department of Chemistry, University of Cambridge, Cambridge, UK
[2] School of Geography, Earth and Environmental Sciences, University of Birmingham, UK

* Corresponding author: markus.kalberer@atm.ch.cam.ac.uk

Atmospheric aerosol particles are important in many atmospheric processes such as light scattering, light absorption, and cloud formation. Oxidation reactions continuously change the chemical composition of aerosol particles, especially organic components, which are often a dominant fraction and lead to highly complex compound mixtures in ambient aerosols. These ageing processes are poorly understood but are known to affect for example the cloud formation potential of aerosol particles.

The use of conventional analytical techniques often limits a comprehensive characterization of organic aerosol composition and processes due to the thousands of compounds present in organic aerosol particles and the often only small amounts of sample (in the µg range) available for analysis. In addition, organic aerosol components cover a very large chemical space, e.g., with regard to polarity, solubility or functional group distribution. Most conventional analytical separation techniques are selective to a rather narrow section of this large chemical space and thus for conventional analytical techniques a majority of the compounds present in organic aerosol is not accessible due to these fundamental limitations. Mass spectrometry is the only analytical technique that combines sufficient sensitivity and separation power to characterize the complex compound mixtures in organic aerosols. Developments of two instrumental aspects, better mass resolution and novel ionization techniques, contributed to an advanced understanding of atmospheric aerosol composition in recent years and examples of both aspects will be discussed here.

The use of high resolution and ultra-high resolution mass spectrometers allows identifying the elemental composition of thousands of unknown organic compounds and a detailed characterization of particle phase reaction products such as oligomers (1-3). High resolution mass spectrometers are very successfully deployed in field measurements and significantly advanced our qualitative and quantitative understanding of atmospheric aerosol composition and the effect of oxidative aging processes (4). A wide range of novel ionization techniques (e.g., direct desorption electrospray ionization (5)) allows for simplified sample preparation procedures, which potentially lead to less measurement artifacts and higher sample throughput. New ionization techniques such as online extractive electrospray ionization also allow following in detail kinetics of particle phase reactions with high time resolution, which is not possible with conventional techniques.

References

(1) Nizkorodov, S.A et al., *Phys. Chem. Chem. Phys.*, **2011**, 13, 3612–3629.
(2) Reinhardt, A. et al., *Anal. Chem.* **2007**, 79, 4074-4082.
(3) Gallimore, P.J. et al., *Atmos. Chem. Phys.* **2011**, 11, 12181-12195.
(4) Jimenez, J.L. *Science*, **2009**, 326, 1525- 1529.
(5) Roach, P.J. et al., *Anal. Chem.* **2010,** 82, 7979–7986.

Investigation of the Photolysis of Nitric Acid on Surfaces by Using Cavity Ring-Down Spectroscopy and Its Novel Variant

Lei Zhu

Wadsworth Center, New York State Department of Health, and Department of
Environmental Health Sciences, State University of New York, Albany, NY, USA
zhul@wadsworth.org

Nitric acid (HNO_3) is a major atmospheric oxidation product of NO_x. Although its gas-phase photolysis in the troposphere is slow, the photolysis rate for HNO_3 deposited on ground and vegetation surfaces to form HONO and NO_x has been reported to be 1-2 orders of magnitude faster than that in the gas phase. The photolysis of HNO_3 adsorbed on ground surfaces has been proposed as a major daytime source of HONO in low-NO_x environments. To understand the difference between the nitric acid photolysis rate in the gas phase and the rate of photolysis on surfaces, my group[1,2] have determined the UV absorption cross sections of HNO_3 adsorbed on fused silica surfaces in the 290-365 nm region by using Brewster angle cavity ring-down technique. Our study showed that the surface absorption cross sections of HNO_3 are at least two orders of magnitude higher than the cross section values of the nitric acid vapor, in the wavelength region studied. We also directly measured the 308 nm absorption cross sections of HNO_3 on Al surfaces and on ice films[3] with a complementary technique, and compared the HNO_3 cross section values on various surfaces. My group have investigated the photolysis of nitric acid on aluminum surfaces,[3] on ice films,[3] and on fused silica surfaces,[4] by using excimer laser photolysis at 308 nm combined with cavity ring-down spectroscopy or with Brewster angle cavity ring-down spectroscopy. We have determined the quantum yields of NO_2* (electronically-excited NO_2) from the HNO_3 photolysis on aluminum surfaces, on ice films, and on fused silica surfaces, and examined the dependence of the photolysis quantum yields on surface types.

References

(1) Zhu, C.; Xiang, B.; Zhu, L.; Cole, R. *Chem. Phys. Lett*. **2008**, 458, 373.
(2) Du, J.; Zhu, L. *Chem. Phys. Lett*. **2011**, 511, 213.
(3) Zhu, C.; Xiang, B.; Chu, L. T.; Zhu, L. *J. Phys. Chem. A*, **2010**, 114, 2561.
(4) Abida, O.; Du, J.; Zhu, L. *Chem. Phys. Lett*. **2012**, in press.

Low temperature kinetic studies of atomic nitrogen – radical reactions

Julien Daranlot,[1] Astrid Bergeat,[1] and Kevin M. Hickson[1,*]

[1] Université de Bordeaux, Institut des Sciences Moléculaires, CNRS, UMR 5255, F-33400 Talence, France
km.hickson@ism.u-bordeaux1.fr

In the interstellar medium, and mainly in dark clouds, the chemistry of atomic nitrogen differs from atomic carbon and oxygen because it cannot form more complex hydride species through reaction with H_3^+ [1]. Instead, atomic nitrogen is thought to react mostly with neutral species which involves the conversion from atomic to molecular nitrogen. Four reactions are implicated in this conversion:

$N + OH \rightarrow NO + H$ [1] followed by $N + NO \rightarrow N_2 + O$ [2]

$N + CH \rightarrow CN + H$ [3] followed by $N + CN \rightarrow N_2 + C$ [4]

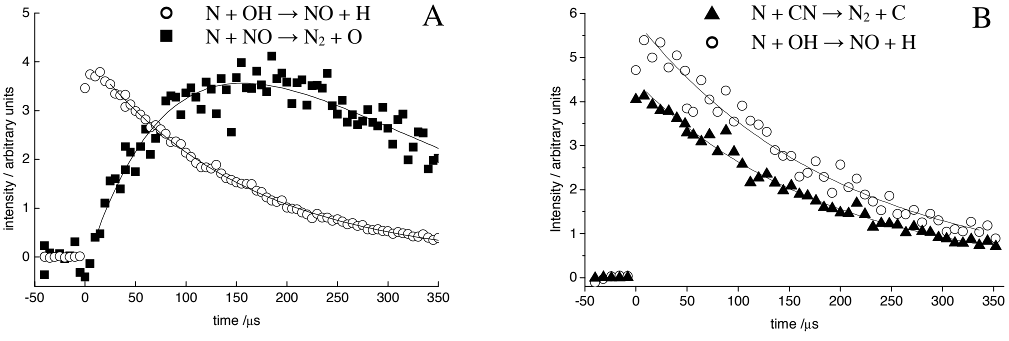
Current models using estimated rates for these reactions predict large abundances of N_2 (10^{-5} with respect to total hydrogen). In contrast, N_2 abundances inferred from observations of N_2H^+ are much lower (10^{-6} with respect to total hydrogen).

The measurement of low temperature rate constants for such atom-radical reactions represents a considerable challenge for experimentalists. A new technique to measure rate constants for reactions between two unstable radicals at low temperatures has been developed. The CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) technique has been coupled with microwave discharge methods to produce excess quantities of ground state atomic nitrogen and PLP-LIF (Pulsed Laser Photolysis – Laser Induced Fluorescence) has been employed to produce and follow the decay of the minor reagents (see figures). The relative rate technique has been employed to extract absolute rate constants using known reference reactions.

We will present kinetic results obtained for the reactions of atomic nitrogen with OH [1] [2], CH [3] and CN [4] over the range $56 \leq T/K \leq 296$.

References

(1) Milligan, D. B.; Fairley, D. A.; Freeman, C. G.; McEwan, M. J. *Int. J. Mass Spectrom.* **2000**, *202*, 351.
(2) Daranlot, J.; Jorfi, M.; Xie, C.; Bergeat, A.; Costes, M.; Caubet, P.; Xie, D.; Guo, H.; Honvault, P.; Hickson, K. M. *Science* **2011**, *334*, 1538.



Typical decays obtained at 56 K. A: OH signal, open circles; NO signal, solid squares. B: OH signal, open circles; CN signal, solid triangles.

Ignition Quality Tester (IQT): An Alternative for Characterizing Combustion Kinetics of Low Volatility Fuels

Eric Osecky,[1] Gregory Bogin,[1] Matthew A. Ratcliff,[2] Jon Luecke,[2] J.Y. Chen[3], Bradley T. Zigler,[2] and Anthony M. Dean[1,*]

[1] Colorado School of Mines, Golden, CO, USA
[2] National Renewable Energy Laboratory (NREL), Golden, CO, USA
3 University of California at Berkeley, Berkeley, CA, USA
* Corresponding author: amdean@mines.edu

The Ignition Quality Tester (IQT) (cf. Figure 1) is a constant volume spray combustion system that can be heated and pressurized to conditions that are similar to a diesel engine at top dead center. The IQT can be viewed as a bridge between engine studies and traditional methods for characterizing combustion kinetics. Because there are no moving parts (e.g. piston) inside the combustion chamber the system is much easier to model than an engine. Also, since the fuel is injected into the chamber as a liquid, studies can be performed on low volatility fuels that are difficult to study with other types of experiments (e.g. shock tubes or rapid compression machines).

By comparing experimental data with model predictions, the IQT can be used to validate kinetic models of ignition. CFD modeling of the IQT using KIVA-3V (using a 42 species mechanism[2]) was used to predict ignition of n-heptane accurately between temperatures of 600-900 K at 15 and 21 bar. While the spray physics effects can affect the ignition results, operating the IQT in a regime where the chemical kinetics dominates allows for the characterization of fuel kinetics. Combustion pressure traces of three isomers of heptane in the IQT are shown in Figure 2. As the heptane isomers become more branched, the boiling point and heat of vaporization decreases causing faster evaporation. This should lead to faster ignition if the evaporation were rate-limiting. Instead, the observed ignition delay increases as the isomers become more branched, indicating that the chemical kinetic effects are dominant.

References

(1) Bogin, G.E.; DeFilippo, A.; Chen, J.Y.; Chin, G.; Luecke, J.; Ratcliff, M. A.; Zigler, B. A.; Dean, A. M. *Energy & Fuels*. **2011**, 25 (12), 5562-5572.
(2) Ra, Y.; Reitz, R. D. *Combust. Flame*, **2008**, 155, 713–738.

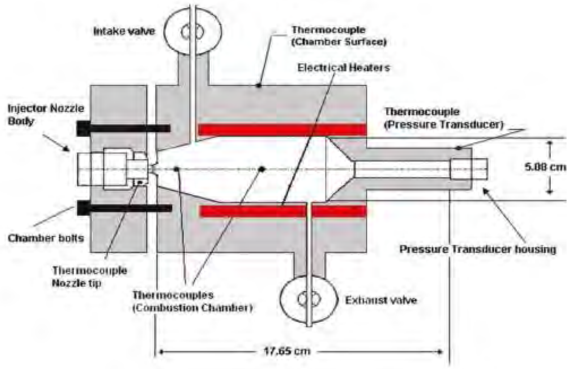


Figure 1. Schematic of IQT combustion chamber[1]

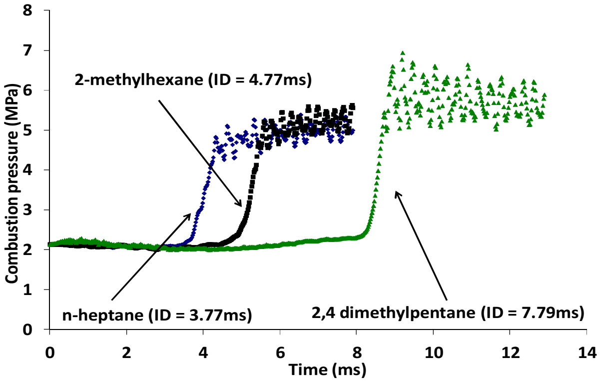


Figure 2. Combustion pressure traces for heptane 2-methylhexane, and 2,4-dimethylpentane: P_{air} = 2.1 MPa, T_{air} = 855 K, averaged over 10 injections[1]

Modeling Chemical Reactions in the 21st Century: Picking the Right Method AND the Right Problem*

Rex T. Skodje

Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, 80309 USA
Rex.Skodje@colorado.edu

Theoretical tools for modeling chemical reactions have become quite highly developed and diverse. This confronts us with many choices in tailoring the theoretical description of a reaction to the requirements of specific applications. We shall review several reactions we have recently treated that required different levels of theory: $F+HCl \rightarrow HF+Cl$ (1), $HO_2+HO_2 \rightarrow H_2O_2+O_2$ (2), $CH_2FOH \rightarrow CH_2O+HF$ (3), and $CH_3OH+HO_2 \rightarrow CH_3O+H_2O_2$ (4). We shall emphasize the role of reactive complexes, torsional motion of the collision complex, and the possibility of water photo-catalysis in the discussion. In addition to selecting the appropriate method to model a given reaction, we also need to face the question of determining which reaction in a given mechanism is the most important to investigate. We shall describe some recent advances in global sensitivity analysis for identifying key reactive steps in large mechanisms.

** Collaborative work, in part, with MJ Davis, V Vaida, L Harding, and K Han*

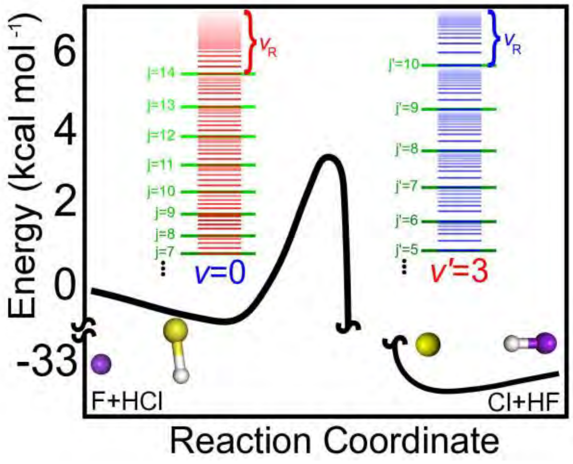
References

(1) R. T. Skodje, "Resonances in Bimolecular Chemical Reactions", Adv. Quantum Chem. 63, 119 (2012).

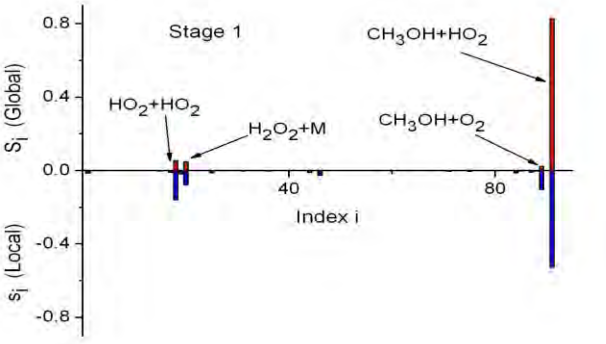
(2) D. D. Y. Zhou, K. L. Han, P. Y. Zhang, L. B. Harding, M. J. Davis, and R. T. Skodje, "Theoretical Determination of the Rate Coefficient for the $HO_2+HO_2 \rightarrow H_2O_2+O_2$ Reaction: Adiabatic Treatment of Anharmonic Torsional Effects", J. Phys. Chem. A, submitted.

(3) Z. C. Kramer, K. Takahashi, and R. T. Skodje, "Water Catalysis and Anticatalysis in Photochemical Reactions: Observation of a Delayed Threshold Effect in the Reaction Quantum Yield", J. Am. Chem. Soc. 132, 15154 (2010).

(4) R. T. Skodje, A. S. Tomlin, S. J. Klippenstein, L. B Harding, and M. J. Davis, "Theoretical Validation of Chemical Kinetic Mechanisms: Combustion of Methanol", J. Phys. Chem. A. 114, 8286 (2010).



Resonance structure of the F+HCL reaction



Global sensitivity analysis of methanol combustion

Product branching of the 2-hydroxyethyl radical intermediate of the OH + ethene reaction

Caroline C. Womack,[1] Britni J. Ratliff,[1] Laurie J. Butler,[1,*] Shih-Huang Lee,[2] Jim Jr-Min Lin[3]

[1] The James Franck Institute and the Department of Chemistry, University of Chicago, Chicago IL, 60637, USA
[2] National Synchrotron Radiation Research Center, Hsinchu, 30076 Taiwan, Republic of China
[3] Institute of Atomic and Molecular Sciences, Academica Sinica, Taipei 10617 Taiwan, Republic of China
* Corresponding author: L-Butler@uchicago.edu

The OH + ethene reaction has been studied extensively, due to the prevalence of hydroxyl radicals in atmospheric and combustion chemistry. While the abstraction pathway leading to H_2O + C_2H_3 is known to dominate at high temperatures, the addition pathway, which proceeds via the CH_2CH_2OH radical intermediate, plays a significant role in the overall dynamics of the reaction at lower temperatures. In an effort to characterize the product branching of the OH + ethene reaction following this addition pathway, we photodissociated two halogenated precursors of the radical intermediate, $BrCH_2CH_2OH$ and $BrCD_2CD_2OH$ at 193 nm to generated highly internally excited 2-hydroxyethyl radicals.[1-3] Using a crossed laser-molecular beam scattering apparatus with tunable photoionization detection, and a velocity map imaging apparatus with VUV photoionization, we detected the products of the major primary photodissociation channel (Br and CH_2CH_2OH/CD_2CD_2OH), and of the secondary dissociation of the excited radicals.

We present results on an unexpected product channel of the 2-hydroxyethyl radical, the water + vinyl channel. The velocity distribution of the signal at $m/e = 27$ (or $m/e = 30$) allows us to identify signal from vinyl (C_2H_3 or C_2D_3) product, assigned to a frustrated dissociation toward OH + ethene followed by H- or D-atom abstraction. We compare these results to predictions from statistical transition state theory and prior classical trajectory calculations on the OH + ethene potential energy surface that evidenced a roaming channel to produce water + vinyl products. Surprisingly, the branching fraction to this channel is similar in the deuterated and non-deuterated systems and thus the larger than predicted branching to this channel may not be due to quantum tunneling. Rather, we consider how the branching to the water + vinyl channel might be sensitive to the angular momentum of the β-hydroxyethyl radicals.

References

(1) Ratliff, B. J.; Womack, C. C.; Tang, X. N.; Landau, W. M.; Butler, L. J.; Szpunar, D. E. *J. Phys. Chem. A* **2010**, *114*, 4934.
(2) Ratliff, B. J.; Alligood, B. W.; Butler, L. J.; Lee, S.-H.; Lin, J. J. M. *J. Phys. Chem. A* **2011**, *115*, 9097.
(3) Womack, C. C.; Booth, R. S.; Brynteson, M. D.; Butler, L. J.; Szpunar, D. E. *J. Phys. Chem. A* **2011**, *115*, 14559.

The OH + CO Reaction System: *ab initio* SCTST Rate Constants and Semi-Empirical Master Equation Models

John R. Barker,[1,*] Thanh Lam Nguyen,[2] Bert C. Xue,[2] Ralph E. Weston, Jr.,[3] and John F. Stanton [2]

[1] University of Michigan, Ann Arbor, MI, USA
[2] University of Texas, Austin, TX, USA
[3] Brookhaven National Laboratory, Upton, NY, USA
* Corresponding author: jrbarker@umich.edu

The OH + CO reaction system is of great importance both in combustion and in the atmosphere. It has also become a benchmark for kinetics, dynamics, and electronic structure calculations.[1] It is convenient for this purpose because all of the individual reaction steps have intrinsic energy barriers (the problems associated with barrier-less reactions can be avoided), isomerization reactions occur, quantum mechanical tunneling is important, and pre-reactive complexes are present, some of which involve hydrogen bonding. In other words, it is a microcosm that contains many of the features found in much larger reaction systems.

We will describe our calculations using Semi-Classical Transition State Theory (SCTST),[1] which was originally developed by W. H. Miller and colleagues,[2] as implemented by some of us[3] and distributed as part of the MultiWell package.[4] Harmonic vibrational frequencies, vibrational anharmonicities, and rotational constants were calculated using the highly accurate CCSD(T) level of theory with large basis sets, as implemented in CFOUR.[5] Another key feature is that relative energies were computed using the *ab inito* HEAT-345Q protocol,[6] which is known to produce energies better than 1 kJ mol^{-1}. For the master equation calculations, the parameters associated with collision frequency and energy transfer were estimated and adjusted to give reasonable agreement with the pressure effects observed in experiment near 300 K. The resulting semi-empirical master equation model calculations, carried out using the MultiWell package,[3] are in good agreement with the pressure-dependent experimental data at $T \geq 300$ K. At $T < 300$ K, the accuracy decreases from semi-quantitative to qualitative, probably as a result of small errors in the *ab initio* energies and other factors, as will be discussed.

References

(1) Nguyen, T. L.; Xue, B.; Weston, R. E., Jr.; Barker, J. R.; Stanton, J. F. *J. Phys. Chem. Letters* **2012**, 3, 1549–1553 and referenced cited therein.
(2) Hernandez, R.; Miller, W. H. *Chem. Phys. Lett.* **1993**, 214, 129-136; Miller, W. H. *Faraday Discuss. Chem. Soc.* **1977**, 62, 40-46; Miller, W. H.; Hernandez, R.; Handy, N. C.; Jayatilaka, D.; Willets, A. *Chem. Phys. Letters* **1990**, 172, 62-68.
(3) Nguyen, T. L.; Stanton, J. F.; Barker, J. R. *Chem. Phys. Letters* **2010**, 499, 9-15; Nguyen, T. L.; Stanton, J. F.; Barker, J. R. *J. Phys. Chem. A* **2011**, 115, 5118–5126.
(4) Barker, J. R.; Ortiz, N. F.; Preses, J. M.; Lohr, L. L.; Maranzana, A.; Stimac, P. J.; Nguyen, T. L.; Kumar, T. J. D. MultiWell-2011.3 Software; J. R. Barker, University of Michigan: Ann Arbor, Michigan, USA (http://aoss.engin.umich.edu/multiwell/), 2011.
(5) Stanton, J. F.; et al. MOLECULE; Almlof, J.; Taylor, P. R. PROPS; Taylor, P. R. ABACUS; Helgaker, T.; et. al., CFour; 2009; http://www.cfour.de.
(6) See Ref. 1 for literature citations.

Revisiting the Thermal Decomposition of CH_3CHO

R. Sivaramakrishnan,[1,*] J. V. Michael,[1] L. B. Harding,[1] and S. J. Klippenstein[1]

[1] Argonne National Laboratory, IL, USA
* Corresponding author: raghu@anl.gov

CH_3CHO thermal decomposition has been a subject of numerous studies over the past 80 years with the essential mechanistic features remaining largely unchanged from the early propositions of Rice and Herzfeld [1]. Initiation through C-C bond fission is the only active channel considered in low temperature [2] or high temperature studies [3]. However, this well characterized decomposition has merited renewed scrutiny in the combustion and gas phase chemical physics community for two main reasons.

1. This is an intermediate that appears in copious amounts when combusting new generation oxygenated fuels, as such or in blends, with conventional fuels [4].
2. Recent experimental [5,6] and theoretical [7] studies have suggested new mechanistic thermal decomposition pathways not considered in prior literature studies.

Recent shock-tube experiments from our laboratory [5] were prompted by the observations of an active “roaming” mechanism forming molecular products (CH_4 + CO) in the photodissociation of CH_3CHO [8]. These experiments utilized ultra-sensitive H-ARAS with very dilute $[CH_3CHO]_0$ and determined yields of H-atom forming channels to be ~ 0.8. With the aid of high-level electronic structure calculations, theoretical kinetics predictions were in quantitative agreement with experiment and indicated that the H-atom yield was only due to C-C bond fission and the non H-atom yield was primarily due to the “roaming” mechanism. However, recent pyrolysis studies on protonated and deuterated acetaldehyde in a micro-tubular reactor by Vasiliou et al. [6] question the validity of the proposed “roaming” mechanism based on observations of vinyl alcohol, ketene, acetylene, and water using sensitive detection techniques. CH_2CHOH is proposed to be a dominant intermediate in this study [6] with subsequent products being produced from unimolecular reactions of CH_3CHO and CH_2CHOH.

In this work we have refined the sub-mechanism for acetaldehyde pyrolysis as part of ongoing modeling efforts on ethanol combustion. The C_2H_4O and C_2H_5O potential energy surfaces have been revisited with theoretical kinetics predictions for relevant channels in acetaldehyde and vinyl alcohol. The present theoretical predictions indicate a minor role for vinyl alcohol in CH_3CHO decomposition in accord with our recent experiments [5] and theory [7]. Modeling indicates that the observations of ketene, acetylene, and water in the recent study of Vasiliou [6] are due to secondary reactions and have no bearing on the initiation steps for CH_3CHO decomposition.

References

(1) Rice, F.O.; Herzfeld, K.F. *J. Amer. Chem. Soc.* **1934**, 56, 284-289.
(2) Laidler, K.J.; Liu, M.T.H. *Proc. Roy. Soc. Lon. A* **1967**, 297, 365-375.
(3) Gupte, K.S.; Kiefer, J.H.; Tranter, R.S.; Klippenstein, S.J.; Harding, L.B. *Proc. Combust. Inst.* **2007**, 31, 167-174.
(4) Kohse-Höinghaus, K.; Oßwald, P.; Cool, T.A.; Kasper, T.; Hansen, N.; Qi, F.; Westbrook, C.K.; Westmoreland, P.R. *Angew. Chem. Int. Ed.* **2010**, 49, 3572-3597.
(5) Sivaramakrishnan, R.; Michael, J.V.; Klippenstein, S.J. *J. Phys. Chem. A* **2010**, 114, 755.
(6) Vasiliou, A.; Piech, K.M.; Zhang, X.; Nimlos, M.R.; Ahmed, M.; Golan, A.; Kostko, O.; Osborn, D.L.; Daily, J.W.; Stanton, J.F.; Ellison, G.B. *J. Chem. Phys.* **2011**, 135, 014306.
(7) Harding, L.B.; Georgievskii, Y.; Klippenstein, S.J. *J. Phys. Chem. A* **2010**, 114, 765-777.
(8) Houston, P. L.; Kable, S. H. *Proc. Nat. Acad. Sci.* **2006**, *103*, 16079.

What is new on the mode-specific and bond-selective chemistry in bimolecular reactions?

Kopin Liu

Institute of Atomic and Molecular Sciences (IAMS), Academia Sinica, P. O. Box 23-166, Taipei, Taiwan 10617

This talk will highlight our recent studies on the reaction of atoms/radicals with stretch-excited methane isotopomers. The experiments were performed under crossed-beam conditions, using a time-sliced, ion velocity-imaging detection scheme, which enables us to acquire the quantum-state correlation of the coincidently formed product pairs [1,2]. Such product pair-correlation measurements can reveal dynamics information that are often hidden or lost by conventional measurements [3]. To explore the mode-specific and bond-selective reactivity, a narrowband IR OPO/OPA was used to prepare the stretch-excited methane reactants [4-8]. A number of fundamental issues in reaction dynamics will be elucidated when compared to the ground state reactivity. In particular, a conceptual framework that links the mode-selective chemistry to the stereo-specific reactivity will be proposed, which in turn leads to a complementary view of the Polanyi's rules [9,10] from different perspective. More recently, the polarization property of the IR pumping laser was exploited to actively control the reaction outcomes in stretch-excited reactions [11].

References

(1) J. J. Lin, J. Zhou, W. Shiu, K. Liu, Rev. *Sci. Instrum*. **2003**, 74, 2495-2500.
(2) J. J. Lin, J. Zhou, W. Shiu, K. Liu, *Science* **2003**, 300, 966-969.
(3) K. Liu, *Phys. Chem. Chem. Phys*. **2007**, 9, 17-30.
(4) S. Yan, Y.-T. Wu, K, Liu, *Science* **2007**, 316, 1723-1726.
(5) J. Riedel, Y. Yan, H. Kawamata, K. Liu, *Rev. Sci. Instrum*. **2008**, 79, 033105.
(6) S. Yan, Y.-T. Wu, K, Liu, *PNAS* **2008**, 105, 12667-12672.
(7) W. Zhang, H. Kawamata, K. Liu, *Science* **2009**, 325, 303.
(8) F. Wang, K. Liu, Chem. *Science* **2010**, 1, 126-133.
(9) J. C. Polanyi, *Acc. Chem. Res*. **1972**, 5, 161.
(10) J. C. Polanyi, *Science* **1987**, 236, 680.
(11) F. Wang, J.-S. Lin, K. Liu, *Science* **2011**, 331, 900-903.

The F + H_2 reaction at very low temperatures

Meryem Tizniti,[1] Sébastien D. Le Picard, [1,*] François Lique,[2] André Canosa and Ian R. Sims[1,*]

[1] Institut de Physique de Rennes, UMR CNRS-UR1 6251, Université de Rennes 1, 263 Avenue du Général Leclerc, 35042 Rennes Cedex, France
[2] LOMC – Université du Havre, 25 Rue Philippe Lebon, BP 540 – 76 058 Le Havre Cedex, France
* Corresponding authors: sebastien.le-picard@univ-rennes1.fr, ian.sims@univ-rennes1.fr

The use of the CRESU (a French acronym for Reaction Kinetics in Uniform Supersonic Flow) technique coupled with pulsed laser photochemical kinetics methods (1) has shown that radical-radical, radical-unsaturated molecule and even radical-saturated molecule reactions can be rapid down to the temperatures of dense interstellar clouds (10—20 K), and the results have had a major impact in astrochemistry and planetology, as well as proving an exacting test for theory (2). Rate coefficients have been measured as low as 5.8 K for the reaction $S(^1D) + H_2$ (3). Until now, all of the fast chemical reactions whose rate coefficients have been measured in this way have taken place on attractive potential energy surfaces with no overall barrier to reaction.

The reaction $F + H_2 \rightarrow HF + F$ has long served as a benchmark for comparison between dynamics and kinetics experiments and quantum scattering calculations (4). It is also believed to be the primary production route for interstellar HF (5). Recent observations by the Herschel space telescope (6) have indicated that HF is the dominant reservoir of interstellar fluorine under a wide range of conditions and has the potential to become an excellent tracer of molecular hydrogen, and provides a sensitive probe of small H_2 column density clouds. However, the F + H_2 reaction possesses a small energetic barrier (~7 kJ mol^{-1}), and around 300 K its rate coefficient falls quite steeply with decreasing temperature. Calculations show, however, that tunnelling plays an increasingly dominant role as the temperature falls, and the rate constant becomes essentially temperature-independent below 20—30 K. The tunnelling calculations are sensitive not only to the barrier height, but also its precise form, with resonances and non-adiabatic effects also playing a strong role (7).

In this contribution, we will present completely new experimental measurements of the rate coefficient for the F + H_2 reaction at temperatures between 10 K and 300 K, along with a detailed comparison with new quantum reactive scattering calculations on the new hybrid new hybrid Li-Werner-Alexander-Lique potential surface. The experimental measurements of this rate coefficient, two orders of magnitude slower than typical barrierless reactions at 10 K, necessitated the use of new Laval nozzles operating with pure hydrogen buffer gas. The reaction was initiated by pulsed 248 nm excimer laser photolysis of F_2, and followed in real time by pulsed VUV LIF detection of H-atom products at 121.6 nm.

References

(1) Sims, I. R.et al. *J. Chem. Phys.* **1994**, 100, 4229-4241.
(2) Sabbah, H.et al. *Science* **2007**, 317, 102-105.
(3) Berteloite, C.et al. *Phys. Rev. Lett.* **2010**, 105, 203201.
(4) Hu, W. F.; Schatz, G. C. *J. Chem. Phys.* **2006**, 125, 132301.
(5) Neufeld, D. A.; Wolfire, M. G. *Astrophys. J.* **2009**, 706, 1594-1604.
(6) Neufeld, D. A.et al. *Astron Astrophys* **2010**, 518, L108.
(7) Lique, F.; Li, G.; Werner, H.-J.; Alexander, M. H. *J. Chem. Phys.* **2011**, 134.

Atmospheric Acids as Catalyst for Gas Phase Reactions: CH_3O isomerization and SO_3 hydrolysis

Amitabha Sinha
Department of Chemistry and Biochemistry, University of California-San Diego
La Jolla, California 92093-0314.

The catalytic ability atmospheric acids such as formic and sulfuric acid to facilitate the isomerization of the CH_3O radical to CH_2OH have been studied. It is shown that the activation energy for isomerization are respectively 30.2, 4.2 and 2.3 kcal mol^{-1} when carried out in isolation versus with formic acid and sulfuric acid as catalysts. The formation of a double hydrogen bonded transition state is central to lowering the activation energy and facilitating the intramolecular hydrogen atom transfer that is required for isomerization. The results demonstrate the feasibility of acids catalyzing a thermal gas phase reaction that would otherwise be forbidden.[1] In a second computational study we explore the changes in reaction barrier height for the gas phase hydrolysis of SO_3 to form H_2SO_4 in the presence of a single formic acid (FA) molecule. For comparison, we have also performed calculations for the reference reaction involving water assisted hydrolysis of SO_3 at the same level. Simple kinetic analysis of the relative rates suggests that the reduction in barrier height facilitated by FA, the greater stability of the pre-reactive $SO_3\cdots H_2O\cdots FA$ collision complex compared to $SO_3\cdots H_2O\cdots H_2O$ and the rather plentiful atmospheric abundance of FA, combine to make the formic acid mediated hydrolysis of SO_3 a potentially important pathway for gas phase atmospheric sulfuric acid production.[2]

References:

1. Buszek, R. J.; Sinha, A.; Francisco, J.S; J. Am. Chem. Soc.; **133 ,** 2013-2015 (2011).

2. Hazra, M.K.; Sinha, A.; J. Am. Chem. Soc.; **133 ,** 17444-17453 (2011).

Product detection of the CH radical reactions with acetaldehyde and acetone

Fabien Goulay,[1,*] Adam J. Trevitt,[2] John D. Savee,[3] Jordy Bouwman,[4] David L. Osborn,[3] Craig A. Taatjes,[3] Kevin R. Wilson[4] and Stephen R. Leone[4,5]

[1] West Virginia University, Morgantown, WV, USA
[2] University of Wollongong, Wollongong, Australia
[3] Sandia National laboratories, Livermore, CA, USA
[4] University of California at Berkeley, Berkeley, CA, USA
[5] Lawrence Berkeley National laboratory, Berkeley, CA, USA
* Corresponding author: Fabien.Goulay@mail.wvu.edu

The reaction of methylidyne radical (CH) with carbonyl compounds such as aldehydes, ketones or carboxylic acids is likely to play a central role in the chemical evolution of combustion environments. The CH radical displays very rapid reaction kinetics with formaldehyde[1] and ketene[2] but the general reaction mechanism with carbonyl compounds is unknown. We have studied the reactions of CH with acetaldehyde (CH_3CHO) and acetone (CH_3CH_3CO) at room temperature using a multiplexed photoionization mass spectrometer coupled to the tunable vacuum ultraviolet synchrotron radiation of the Advanced Light Source. Analysis of photoionization yields versus photon energy for the reaction of CH and CD with acetaldehyde and acetone and CH radical with partially deuterated acetaldehyde (CD_3CHO) elicits fine details about the reaction mechanism.

The reaction with acetaldehyde yields five exit channels.[3] The CH_2 elimination channel is found to preferentially form the acetyl radical by removal of the aldehydic hydrogen. The insertion of the CH radical into a C–H bond of the methyl group of acetaldehyde is likely to lead to a C_3H_5O-reaction intermediate that can isomerize by β-hydrogen transfer of the aldehydic hydrogen atom and dissociate to form acrolein + H or ketene + CH_3, which are observed directly. Cyclo-addition of the radical onto the carbonyl group is likely to lead to the formation of the observed products, methylketene ($CH_3CH{=}C{=}O$), methyleneoxirane (c-$H_2C{=}COCH_2$), and acrolein ($H_2C{=}CH$-CHO). The reaction with acetone produces mainly dimethylketene ($CH_3CH_3C{=}C{=}O$) by elimination of the H-atom initially from the radical and methacrolein ($H_2C{=}CCH_3$-CHO) by elimination of an H-atom initially from a methyl-group.

These experimental results suggest that the CH radical can add onto a C=O bond to from cyclic intermediates that further isomerize by ring opening. Elimination of the hydrogen initially from the radical forms substituted ketene molecules while elimination of a hydrogen atom in β-position from the newly inserted carbon atom forms conjugated enal molecules.

References

(1) Zabarnick, S.; Fleming, J. W.; Lin, M. C. *21st Int. Symp. Comb.* **1986**, 713-719.
(2) Hancock, G.; Heal, M. R. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2121-2123.
(3) Goulay, F.; Trevitt, A. J.; Savee, J. D.; Bouwman, J.; Wilson, K. R.; Osborn, D. L.; Taatjes, C. A.; Leone, S. R. *J. Phys. Chem. A* **2011**, 10.1021/jp2113126.

Theoretical Studies of HOCO → H + CO_2

Richard Dawes,[1] Albert Wagner,[2,*] Jun Li,[3] and Hua Guo[3]

[1] Missouri University of Science and Technology, Rolla, MO 65409, USA
[2] Argonne National Laboratory, Lemont, IL, USA
[3] University of New Mexico, Albuquerque, NM, 87131, USA
* Corresponding author: wagner@anl.gov

Recent experimental studies[1] by the Continetti group have concluded that the barrier between HOCO and the dissociated products H+CO_2 is considerably narrower than that represented in previously available potential energy surfaces (PESs).[2] We report here a new global PES for the HOCO system as well as additional electronic structure calculations along a minimum energy path (MEP) of the title reaction channel and initial calculations of the decay of bound HOCO through the barrier to products H+CO_2.

The highest level electronic structure calculations are focused on the reaction path. Calculations at the full-valence MRCI(+Q)/CBS level produce excellent agreement with known thermochemistry. Fortuitously close agreement is also obtained with the much more affordable CASPT2/avdz method using the more restrictive (13e,11o) active space. Harmonic frequencies were computed along the MEP in addition to a cubic force field expanded at the TS.

At the UCCSD(T)-F12b/AVTZ level of electronic structure calculations, a global PES has been developed Guo and coworkers.[3] It also shows a significantly narrower barrier than previous PESs.

The reaction path is used to calculate the rate of decay of cis-HOCO through tunneling by a variety of methods as found in POLYRATE[4] and as recently developed by the Barker-Stanton groups.[5] Both canonical and microcanonical rate constants have been computed using these two approaches and significant tunneling has been found. In addition, the H/D kinetic isotope effects have been obtained. Results will be contrasted with the experimental studies.

References

(1) Johnson, C. J.; Poad, B. L. J.; Shen, B. B., and Continetti, R. E. *J. Chem. Phys.* **2011**, 134, 171106.
(2) For example, Lakin, M.; Troya, D.; Schatz, G.; Harding, L. *J. Chem. Phys.* **2003,** 119, 5848.
(3) Li, J. Wang, Y., Jiang, B., J. Ma, Dawes, R., Xie, D., Bowman, J. M. and Guo, H., *J. Chem. Phys.*, 2012, 136, 041103
(4) POLYRATE web site: http://comp.chem.umn.edu/polyrate/
(5) Nguyen, T. L.; Stanton, J. F.; Barker, J. R. *Chem. Phys. Lett.* 2010, 9, 499

The gas phase reactivity of hydroxyl radical in the atmosphere. Hydrogen atom transfer versus proton coupled electron transfer processes.

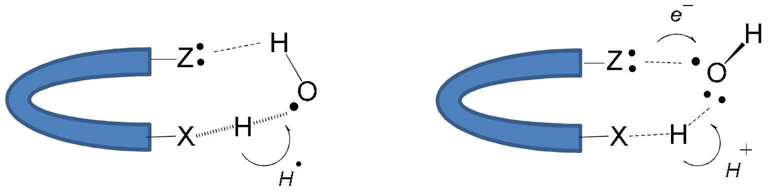
Josep M. Anglada

Departament de Química Biològica i Modelització Molecular, IQAC-CSIC, c/ Jordi Girona, 18 E-08034
Barcelona, Spain e-mail : anglada@iqac.csic.es

Hydroxyl radical is the main oxidant in atmosphere and reacts, in a great part, by abstracting hydrogen atoms from organic species. It is generally accepted that the hydrogen abstraction by hydroxyl radical proceeds by the concerted breaking and forming of the covalent bond as it is indicated in equation 1.

$$X\text{-}H + OH \rightarrow X + H_2O \qquad (1)$$

In this case, the OH radical approaches the X-H bond with its unpaired electron and form the H-OH bond whereas the X-H bond is broken. This process is named hydrogen atom transfer (*hat*) and it is schematized in Figure 1a. It is known that the associated energy barrier is related to the bond dissociation energy of the X-H bond, which depends on the triplet repulsion energy for the X•/OH• pair at the transition structure.[1] Depending on the nature of X (for instance, having a terminal atom Z with a lone pair of electrons) the hydroxyl radical can approach in a different manner to the X-H reactant and react in a different way, undergoing a proton coupled electron transfer (*pcet*) mechanism. This process is schematized in Figure 1b, where an electron is transferred from the lone pair of the Z terminal atom to the oxygen atom of the OH radical, and, simultaneously, the hydrogen atom bonded to X is transferred as a proton to the OH moiety.[2,3]



a) Hydrogen atom transfer **b) Proton coupled electron transfer**

The relevance of the *hat* and *pcet* processes will be studied by considering the oxidation of atmospheric acids by hydroxyl radical, analyzing also the effect of water vapor on the reactivity of these species.[4]

References

(1) A. A. A Zavitsas, J. Am. Chem. Soc. **1998**, 120, 6578.
(2) S. Olivella, J. M. Anglada, A. Solé, J. M. Bofill. Chem. Eur. J., **2004**, 10, 3404.
(3) J. M. Anglada, J. Am. Chem. Soc, **2004**, 126, 9809.
(4) J. González, J. M. Anglada, J. Phys. Chem. A, **2010**, 114,9151

Mario Molina Tribute Session
Oral Wednesday 3:00 – 3:20

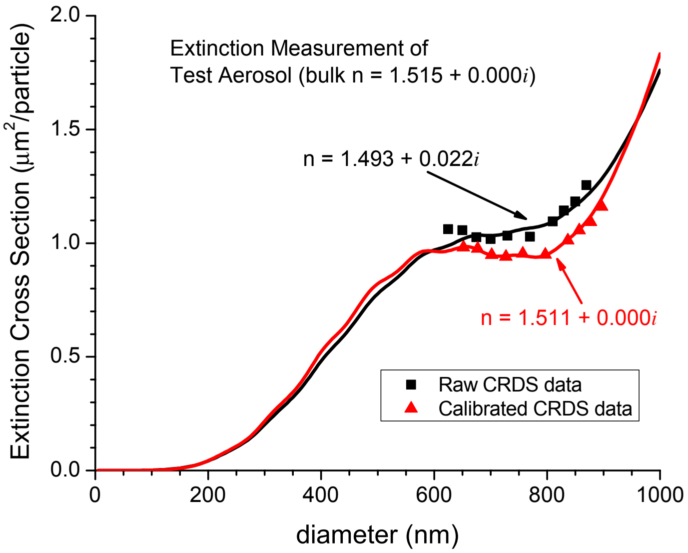
Reducing Uncertainties in Using Cavity Ring-Down Spectroscopy to Measure Aerosol Optical Properties

Justin R. Toole,[1] Lindsay H. Renbaum,[2] and Geoffrey D. Smith[3,*]

[1] Now at the United States Military Academy, West Point, NY, USA
[2] Now at the University of British Columbia, Vancouver, BC, Canada
[3] University of Georgia, Athens, GA, USA
* Corresponding author: gsmith@chem.uga.edu

Cavity Ring-Down Spectroscopy (CRDS) is a highly-sensitive tool for measuring extinction (i.e. absorption and scattering) by gas-phase species as well as aerosols. It has found use in field measurements and increasingly-sophisticated laboratory studies of light absorption and scattering by particles at wavelengths from the UV to the near-IR. It has become possible to use CRDS to examine the influences of particle morphology, coatings and chemical composition on light extinction. However, these influences are often subtle requiring highly-precise and accurate measurements of particle diameter and concentration, and the associated uncertainties can dominate the uncertainties in using CRDS to measure aerosol optical properties.

Here, we present a method for calibrating a CRDS instrument using size-selected aerosols of squalane ($C_{30}H_{62}$), an inert, low-volatility, hydrophobic branched alkane that is liquid at room temperature. Using the known index of refraction of squalane and Lorenz-Mie theory, the distribution of particle sizes selected by the differential mobility analyzer (DMA) and the counting efficiency of the condensation particle counter (CPC) are characterized. This calibration makes it possible to measure particle extinction to within 1% with uncertainties of ± 0.003 on both the real and imaginary parts of the retrieved index of refraction.



Particle extinction cross sections are fit by Lorenz-Mie theory much better when the CRDS instrument is calibrated with squalane (red) compared to when it is not calibrated (black).

Atmospheric Aging of Soot Aerosols

Renyi Zhang

Department of Atmospheric Sciences, College of Geosciences, Department of Chemistry,
College of Science, Center for Atmospheric Chemistry and Environment, Texas A&M University

Soot from incomplete combustion of fossil fuels represents a significant fraction of primary atmospheric aerosols. Because of the high absorption cross-section of BC over a broad range of the solar spectrum, soot contributes significantly to climate change by direct radiative forcing and is the second most important climate-warming agent after carbon dioxide. Atmospheric aging considerably modifies the chemical and physical properties of BC, making them largely independent of the aerosol origin. Aging of BC aerosol occurs through coagulation with other aerosols or by multi-phase interaction with organic and inorganic vapors formed from photochemical oxidation of primary pollutants. BC aerosols may be more absorptive and exerts a higher positive direct radiative forcing. The ability of BC to absorb visible light may be considerably enhanced when BC particles are coated by transparent materials. The increase in light absorption caused by coatings is likely accompanied by an even larger increase in light scattering, which partially compensates the positive forcing of the light absorbing BC core. Currently, the mechanisms responsible for BC aging in the atmosphere remain poorly understood. In this talk, laboratory results and field measurements will be presented to quantify aging of soot particles and the associated changes on their properties, including morphology, hygroscopicity, and optical properties. The implications of soot aging on their impacts on air quality, weather, human health, and climate will be discussed.

Direct Measurement of the reaction of Criegee Intermediates with SO_2

Carl J. Percival,[1] Oliver Welz,[2] Arkke J. Eskola,[2] John D. Savee,[2] David L. Osborn,[2] Dudley E. Shallcross,[3] and Craig A. Taatjes.[2]
[1]School of Earth, Atmospheric and Environmental Sciences, The University of Manchester, Williamson Building, Oxford Road, Manchester M13 9PL, UK
[2]Combustion Research Facility, Sandia National Laboratories, 7011 East Ave., MS 9055, Livermore, California 94551 USA.
[3]School of Chemistry, University of Bristol, Bristol BS8 1TS, UK.
* Corresponding author: carl.percival@manchester.ac.uk

Carbonyl oxides, known as "Criegee intermediates" after Rudolf Criegee, who proposed their participation in ozonolysis,[1] are important species in tropospheric chemistry. Most carbonyl oxides in the troposphere are produced by ozonolysis, but other tropospheric reactions can also produce Criegee intermediates.[2, 3] However, until recently[2, 4] no Criegee intermediate had been observed in the gas phase, and information about the reactivity of Criegee intermediates in gas-phase ozonolysis or in the troposphere have relied on indirect determinations.[5, 6]

In this work, the reactions of the two simplest Criegee intermediates, CH_2OO and CH_3CH_2OO with SO_2 have been measured by laser photolysis / tunable synchrotron photoionization mass spectrometry. Diiodomethane and Diiodoethane photolysis produces RI radicals, which react with O_2 to yield ROO + I, wher R = CH_2 or CH_3CH_2. The Criegee intermediates are reacted with a large excess of SO_2 and both the disappearance of Criegee intermediates and the formation of reaction products are observed by time-resolved photoionization mass spectrometry. Figure 1 shows a second order plot for the reaction of CH_3CH_2OO with SO_2 The final analysis yields rate coefficients at 298 K (and 4 Torr) of $(3.9 \pm 0.7) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for $CH_2OO + SO_2$ and of $(2.4 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for $CH_3CH_2OO + SO_2$.

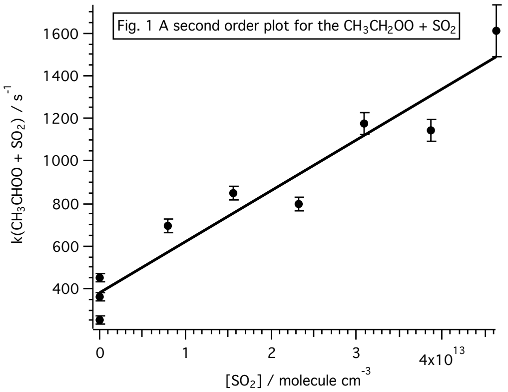


Fig. 1 A second order plot for the $CH_3CH_2OO + SO_2$

The direct determinations of the rate constants for CH_2OO and CH_3CH_2OO with SO_2, are considerably higher than previous estimates. Placing the present results into a tropospheric chemistry model[7] implies a substantial role of Criegee intermediates in sulfate chemistry. Oxidation of SO_2 by CBs will lead to SO_3 that will from H_2SO_4 rapidly on reaction with water. The production of H_2SO_4 via Criegee radical reaction will be at least as important as the OH radical production route. It is well known that sulfuric acid is a key component in the secondary particle formation in the atmosphere and thus this new route to form sulfuric acid could have a significant impact on aerosol formation in the atmosphere.

References

(1) Criegee, R.; Wenner, G. *Liebigs. Ann. Chem.* **1949**, 564, 9.
(2) Welz, O. et al., *Science* **2012**, 335, 204.
(3) Asatryan, R.; Bozzelli, J.W. *Phys. Chem. Chem. Phys.* **2008**, 10, 1769.
(4) Taatjes, C. A. et al., *J. Am. Chem. Soc.*, **2008**, 130, 11883.
(5) Johnson, D.;. Marston, G. *Chem. Soc. Rev.* **2008**, 37, 699.
(6) Donahue, N. M. et al., *Phys. Chem. Chem. Phys.* **2011**, 13, 10848.
(7) Archibald, A.T. *et al.*, *Atmos. Chem. Phys.* **2010**, 10, 8097.

Mario Molina Tribute Session
Oral Wednesday 4:00 – 4:20

Probing complex single particles one at a time: What can we learn about the troposphere?

Kimberly A. Prather,
University of California San Diego

As demonstrated for the stratosphere decades ago, heterogeneous reaction processes can profoundly impact our atmosphere. Over the past several decades, lab studies have shifted their focus from stratospheric to tropospheric reactions on aerosols including dust, soot, organic carbon, and sea salt particles. However, one common challenge in such studies involves replicating the chemical complexity of atmospheric aerosols so the results can be used to explain field observations. Most studies treat the aerosol as an "average" composition comprised of all particle species that are present. However, atmospheric aerosols are comprised of external mixtures of many particle types with different surface properties that will react differently, even for one source such as sea spray. This presentation will focus on results from studies that are now addressing how these different complex particle types react and behave in the atmosphere on an individual basis. New results will be presented from a new ocean-atmosphere lab designed to simulate the complexity of real world sea spray aerosols in a controlled laboratory setting.

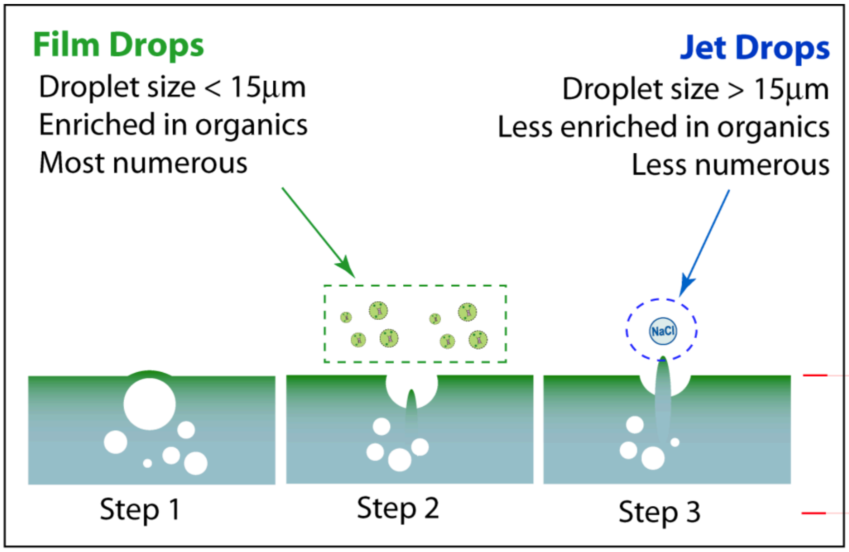


Figure 1. Steps involved in sea spray generation showing how individual particles have different sizes and chemical compositions depending on the bubble bursting production mechanism.

From Atmospheric Chemistry to Science-Policy of Climate Change

Polanyi Lecture, June 20, 2012

Mario Molina

University of California, San Diego, USA
mjmolina@ucsd.edu

Atmospheric chemistry and chemical kinetics have played a central role in our assessment of the impact of human activities on the Earth's atmosphere. Reaction rate constants measured in the laboratory are among the important parameters required for reliable understanding and modeling of the behavior of the atmosphere under natural as well as under conditions perturbed by human activities. Such an understanding has been crucial for society to take the necessary measures to address challenges such as the degradation of air quality in urban centers and stratospheric ozone depletion. Much remains to be done, however, to properly address climate change, the most serious environmental challenge facing society in the 21st century. The International Panel on Climate Change concluded in 2007 that there is more than 90% probability that human activities are causing the observed changes in the Earth's climate in recent decades.

The average temperature of the Earth's surface has increased so far by about 0.8 degrees Celsius since the Industrial Revolution, and the frequency of extreme weather events such as droughts, floods and intense hurricanes is also increasing. The consensus of informed experts is that the risk of causing dangerous changes to the climate system increases rapidly if the average temperature rises more than two or three degrees Celsius. Society faces an enormous challenge to effectively reduce greenhouse gas emissions to avoid such dangerous interference with the climate system. This goal can only be achieved by taking simultaneously measures such as significantly increasing energy efficiency in the transportation, building, industrial and other sectors, using renewable energy sources such as solar, wind, and geothermal, and possibly developing and using safer nuclear energy power plants. Fossil fuels such as coal and petroleum can continue to be used beyond a transition period of about one or two decades, but only as long as the emitted carbon dioxide is sequestered and stored in underground reservoirs such as saline domes.

Gas Kinetics and Sustainable Mobility

T. J. Wallington

Systems Analytics and Environmental Sciences, Research and Advanced Engineering,
Ford Motor Company, Mail Drop RIC-2122, Dearborn, Michigan 48121-2053, USA

The provision of mobility which is sustainable in every sense of the word (environmental, economic, and social) is a major challenge facing society. This talk will describe the contribution of gas kinetics research to progress made in reducing the vehicle contribution to local air quality and stratospheric ozone issues and the current challenge posed by climate change. The potential roles of advanced gasoline/diesel internal combustion engine vehicles (ICEV), hybrid electric vehicles (HEV), plug-in hybrid electric vehicles (PHEV), hydrogen internal combustion vehicles (H2ICE), hydrogen fuel cell vehicles (H2FCV) and gasoline, diesel, biofuel, electricity and hydrogen fuels in providing future personal mobility will be discussed.

Biomass Pyrolysis in a Heated Microtubular Reactor

AnGayle K. Vasiliou,[1, 3] Krzysztof M. Piech,[1] Beth Reed,[1] Xu Zhang,[2] Mark R. Nimlos,[3] Musahid Ahmed,[4] Amir Golan,[4] Oleg Kostko,[4] David L. Osborn,[5] John W. Daily,[6] John F. Stanton,[7] and G. Barney Ellison* [1]

[1] Department of Chemistry & Biochemistry
University of Colorado
Boulder, CO 80309-0215
* Corresponding author: barney@jila.colorado.edu

[2] Jet Propulsion Laboratory
California Institute of Technology
4800 Oak Grove Drive
Pasadena, CA 91109-8099

[3] National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401

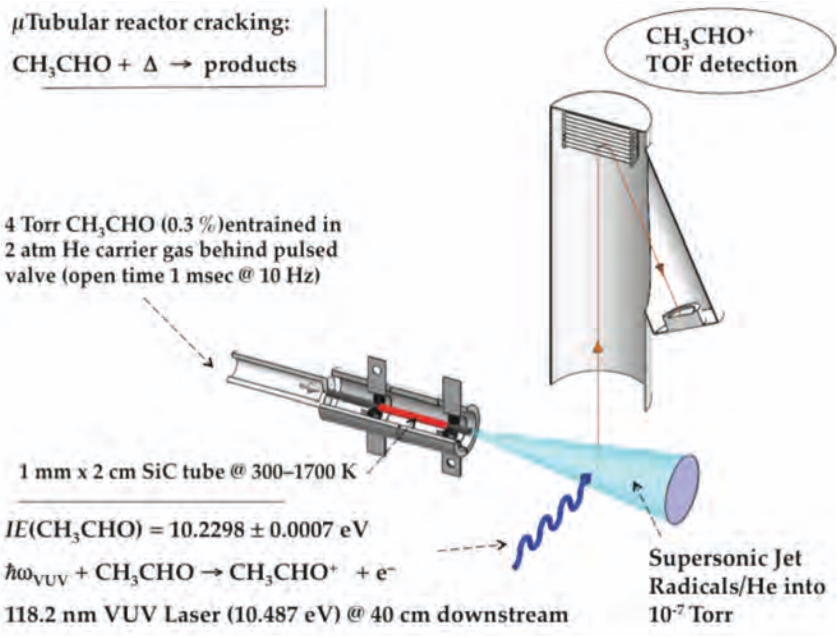
[4] Chemical Sciences Division
LBNL MS 6R-2100
Berkeley CA 94720

[5] Combustion Research Facility
Sandia National Laboratories
PO Box 969 MS 9055
Livermore, CA 94551-0969

[6] Center for Combustion & Env. Research
Department of Mechanical Engineering
University of Colorado
Boulder, CO 80309-0427

[7] Institute for Theoretical Chemistry
Dept. Chemistry, University of Texas
Austin, TX 78712

A heated SiC microtubular reactor has been developed to decompose biomass monomers such as CH_3CHO, C_6H_5OH, $C_6H_5OCH_3$, $HOC_6H_4OCH_3$, $C_6H_5CH_2CH_2OC_6H_5$, and furan. The pyrolysis experiments are carried out by passing a dilute mixture of the organic substrate (roughly 0.1 — 1 %) entrained in a stream of a buffer gas (either He or Ar) through a heated SiC reactor that is 2-3 cm long and 1 mm in diam. Common pressures in the reactor are 50 – 200 Torr and the SiC tube is heated in the range of 1200 — 1900 K. Typical transit times through the reactor are 50 — 200 μsec after which the gas mixture emerges as a skimmed molecular beam at a pressure of approximately 10 μTorr and all chemistry is quenched. The reactor has been deployed in pulsed and CW configurations. In Colorado a pulsed reactor is used because the pyrolysis products are identified by photoionization mass spectroscopy with a 10 Hz YAG laser at $\lambda_0 = 118.2$ nm or 10.487 eV. Separate experiments use matrix infrared absorption spectroscopy to identify the pyrolysis products and to confirm the assignments of the PIMS. In Calif. a CW reactor is used because a CW synchrotron is used as the light source for the PIMS. The pyrolysis of CH_3CHO will be discussed. We observe CH_3CHO (+M) → CH_3 + H + CO + $CH_2{=}C{=}O$, $CH_2{=}CHOH$, $HC\equiv CH + H_2O$.



Low-temperature oxidation chemistry of 1-butanol: A combined photoionization mass spectrometry and quantum-chemical/master-equation study

Oliver Welz,[1,*] Judit Zádor,[1] John D. Savee,[1] Leonid Sheps,[1] David L. Osborn,[1] Stephen J. Klippenstein,[2] and Craig A. Taatjes[1]

[1] Combustion Research Facility, Sandia National Laboratories, MS 9055, Livermore, CA 94551-0969, USA
[2] Chemical Sciences and Engineering Division, Argonne National Laboratories, Argonne, IL 60439, USA
* Corresponding author: onwelz@sandia.gov

The efficient use of novel biofuels in internal combustion engines, particularly those relying on compression ignition, depends critically on an understanding of their fundamental autoignition chemistry. 1-Butanol is a particularly promising candidate as a next-generation biofuel. Whereas its high-temperature ($T > 1000$ K) oxidation has been the subject of substantial experimental and modeling effort, the oxidation chemistry of 1-butanol in particular, and medium-chain alcohols in general, remains underexplored in the low-temperature region ($T < 800$ K), where fuel-chemistry effects on the autoignition behavior are important.

We present a combined experimental and theoretical approach to gain detailed insight into the fundamental low-temperature oxidation chemistry of 1-butanol. On the experimental side, we employ the technique of pulsed laser-photolytic chlorine initiation in a slow-flow reactor between 300 and 700 K at low pressure (~4 Torr). Four different (α-, β-, γ-, and δ-) 1-hydroxybutyl radicals are prepared via H-abstraction by Cl atoms at the different CH sites from 1-butanol. The chemistry of these 1-hydroxybutyl radicals in an excess of O_2 is interrogated using multiplexed time-resolved synchrotron photoionization mass spectrometry. By employing synchrotron radiation as the ionizing source, branching ratios between the observed primary products are obtained on an isomer-resolved level. Relevant stationary points on the potential energy surfaces for the four 1-hydroxybutyl radicals reacting with O_2 have been computed using the CBS-QB3 method, and time-dependent master-equation calculations have been performed based on these surfaces. From the master-equation calculations, product branching ratios for the four 1-hydroxybutyl radical isomer + O_2 reactions are obtained, which are compared to the experimentally derived values.

Our experimental and theoretical results show that the reactions of all four 1-hydroxybutyl radicals with O_2 are dominated by alcohol-specific product channels. We will highlight this observation and the differences from the oxidation chemistry of alkanes. Furthermore, we will discuss the competition between channels associated with chain-propagating formation of OH and essentially chain-terminating channels associated with HO_2 formation.

This work is supported by the Division of Chemical Sciences, Geosciences, and Biosciences, the Office of Basic Energy Sciences, and the U.S. Department of Energy, in part under the Argonne-Sandia Consortium on High-Pressure Combustion Chemistry, (ANL FWP # 59044; SNL FWP # 014544). Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the National Nuclear Security Administration under contract DE-AC04-94-AL85000.

Detailed Kinetic Model for *Iso*-Butanol Pyrolysis and Combustion

Shamel S. Merchant,[1,*] Everton Fernando Zanoelo,[2] Nils Hansen,[3] Kevin M. Van Geem[4] and William H. Green Jr.[1]

[1] Department of Chemical Engineering, Massachusetts Institute of Technology (MIT), Cambridge, MA, USA
[2] Federal University of Paraná (UFPR), Curitiba, PR, Brazil
[3] Combustion Research Facility, Sandia National Laboratories, Livermore, CA, USA
[4] Laboratory of Chemical Technology, Univ. Ghent, Ghent, Belgium
* Corresponding author: shamel@mit.edu

Despite the extensive use of ethanol as a renewable transportation fuel, it is believed that it is not the ideal alternative to gasoline (1, 2). Higher chain alcohols (C3-C5) are considered best options because they have higher energy densities, lower vapor pressures and lower hygroscopicity, with several practical positive effects on combustion engines (2-4). *Iso*-butanol not only presents all the aforementioned advantages when compared to ethanol, but its "production process has already reached near-industrial level" (4).

In the current investigation we present a comprehensive kinetic mechanism for iso-butanol combustion. The kinetic mechanism is generated using the open source software package Reaction Mechanism Generator (RMG) and includes pressure-dependent kinetics. The mechanism is tested against a large number of new and recently published data including – pyrolysis product profiles in plug flow reactor and shock tube, jet-stirred reactor mole fraction profiles, opposed flow diffusion flame mole fraction profiles, laminar flame speeds at different pressures and autoignition delays in rapid-compression machine and high-pressure shock tubes. The isobutanol model predicts with great fidelity on all the above mentioned datasets – ignition delays and major product species are predicted within a factor of two in most cases, for low pressure flame the major radicals are within a factor of three of experimental measurements. A flux and sensitivity analysis is performed for the different datasets to reveal important pathways; of note is the pathway for keto-enol tautomerization in low pressure flames. It is seen in order to reasonably predict the keto- enol product distribution in low pressure flames it is essential to include accurate pressure dependent kinetics for direct and assisted tautomerization for various isomers in the model. To the author's knowledge this is one of the first mechanisms to accurately predict iso-butanol combustion over a wide range of conditions.

References

(1) Atsumi, S.; Hanai, T.; Liao, J.C. *Nature* **2008**, 451, 86-90.
(2) Grana, R.; Frassoldati, A.; Faravelli, T.; Niemann, U.; Ranzi, E.; Seiser, R.; Cattolica, R., Seshadri, K. *Combust. Flame* **2010**, 157, 2137-2154.
(3) Moss, J.T.; Berkowitz, A.M.; Oehlschlaeger, M.; Biet, J.; Warth, V.; Glaude, P.; Battin-Leclerc, F. *J. Phys. Chem. A* **2008**, 112, 10843-10855.
(4) Connor, M.R.; Liao, J.C. *Curr. Opin. Biotech.* **2009**, 20, 307-315.

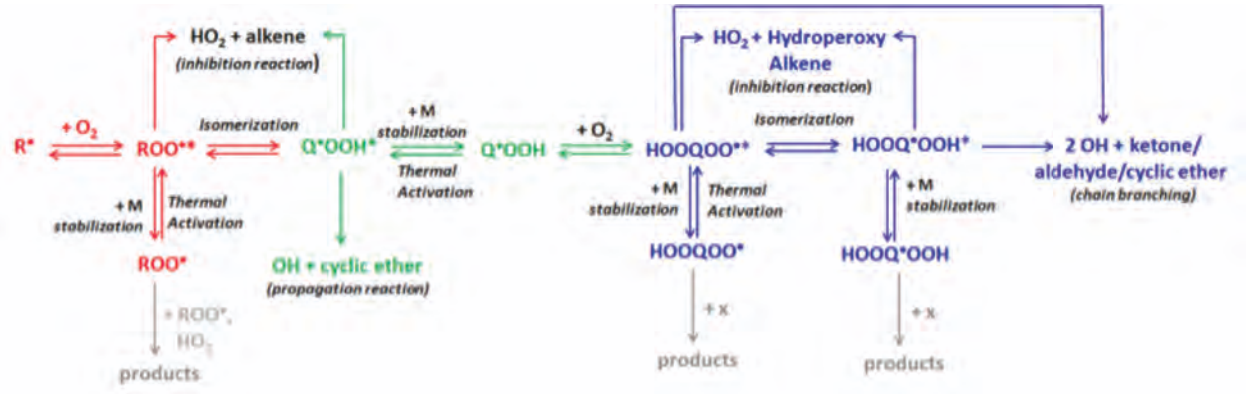
Free Radical Kinetics of Alternative Fuels: From Diesel Ignition to Biocorrosion

Anthony M. Dean

Colorado School of Mines, Golden, CO, USA
amdean@mines.edu

The improved understanding of elementary chemical reactions has markedly improved our ability to describe “real-world” systems. Such approaches require development of accurate, detailed chemical mechanisms, which in turn require careful analysis of different types of elementary reactions. This talk will describe our approach to the characterization of elementary reactions, the construction of detailed mechanisms, and the application to several systems, ranging from hydrocarbon oxidation to biocorrosion. We will focus on the development of rate rules for various types of free radical reactions and discuss how these can then be applied to begin the understand the impact of introducing various types of alternative fuels.

One such system involves the reactions of peroxy and hydroperoxy alkyl radicals[1]. High pressure rate constant estimation rules for the reactions of RO_2 and QOOH are derived from a systematic investigation of sets of reactions within a given reaction class using electronic structure calculations performed at the CBS-QB3 level of theory. Pressure-dependent rate constants can then be calculated and incorporated into mechanisms to predict the impact of various fuel structures on ignition in diesel engines.



Peroxy radical reactions that important for hydrocarbon ignition

---

[1] Villano, S. M.; Huynh, L. K.; Carstensen, H.-H.; Dean, A. M. J. Phys. Chem. A 2011, **115**, 13425–13442.

Experiment and Theory on methylformate and methylacetate kinetics at high temperatures: Rate constants for H-atom abstraction and thermal decomposition

S. Peukert, R. Sivaramakrishnan*, M.-C. Su, and J. V. Michael*

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

Biodiesel is a prevalent alternative that can be used as a neat fuel or in blends with conventional fuels. It offers substantial emissions advantages in compression ignition engines (1,2). Methyl ester combustion chemistry has therefore been the subject of experimental and modeling studies over the past few years (3,4). It is interesting to note though that little attention has been devoted to experimentally understanding the elementary kinetics of even the simplest methyl esters despite this intense activity aimed at understanding the combustion chemistry. This is the motivation for the present study on the title reactions.

The shock tube technique was used to study the high temperature thermal decomposition of methylformate (MF) and methylacetate (MA). The formation of H-atoms was measured behind reflected shock waves by using atomic resonance absorption spectrometry (ARAS). The experiments span a T-range of 1194 – 1371 K at pressures ~ 0.5 atm. The H-atom profiles were simulated using a detailed chemical kinetic mechanism for MF and MA thermal decomposition. The simulations were used to derive rate constants for sensitive decomposition and H-abstraction reactions in MF and MA. In methylformate, the most sensitive reactions that determine H-atom profiles are $CH_3OC(O)H \rightarrow HCO_2 + CH_3$ (A) and $CH_3OC(O)H + H \rightarrow CH_3OCO + H_2$ (B), where H is formed from $HCO_2 \rightarrow H + CO_2$. In methylacetate the most sensitive reactions affecting H-atom formation are $CH_3OC(O)CH_3 \rightarrow CH_3 + OC(O)CH_3$ (C) and $CH_3OC(O)CH_3 + H \rightarrow CH_2OC(O)CH_3 + H_2$ (D). Minor sensitivity was observed for the energetically higher lying bond fission, $CH_3OC(O)CH_3 \rightarrow CH_3 + CH_3OCO$ (E) and H-atom abstraction from MA by CH_3. In MA, H-atoms are formed from CH_3 radicals (through $CH_3 + CH_3 \rightarrow C_2H_4 + 2H$) generated primarily through the C-O bond fission channel (C) with minor contributions from (E). A master equation analysis was performed using CCSD(T)/cc-pv∞z//B3LYP/6-311++G(d,p) energetics and molecular properties for all thermal decomposition processes in MF and MA. The theoretical predictions were found to be in good agreement with the present experimentally derived rate constants for the bond fissions. TST calculations employing CCSD(T)/cc-pv∞z//MP2/aug-cc-pvtz energies and molecular properties for reactions (B) and (D), the only sensitive abstraction processes in MF and MA, are in good agreement with the experimental rate constants. To our knowledge this is the first study providing experimentally derived rate constant values for the primary bond fission and abstraction reactions in MF and MA.

References

(1) Graboski, M. S.; McCormick, R. L. *Prog. Energy Combust. Sci.* **1998**, 24, 125-164.
(2) Agarwal, A. K. Prog. *Ener. Combust. Sci.* **2007**, 33, 233-271.
(3) Kohse-Hoeinghaus, K.; Osswald, P. Cool, T. A.; Kasper, T., Hansen, N.; Qi, F.; Westbrook, C. K.; Westmoreland, P. R. *Angew. Chem. Int. Ed.* **2010**, 49, 3572- 3597.
(4) Lai, J. Y. W.; Lin, K. C.; Violi, A. *Prog. Energy Combust. Sci.* **2011**, 37, 1-14

Pyrolysis of 2,5-Dimethylfuran – Shock Tube Study and Kinetic Modeling

Philipp Friese,[1] Tobias Bentz,[1] Lena Genthner,[1] Johannes Kiecherer,[1]
John Simmie,[2] and Matthias Olzmann[1,*]

[1] Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany
[2] Combustion Chemistry Centre, NUI Galway, Ireland
* Corresponding author: matthias.olzmann@kit.edu

2,5-dimethylfuran (25DMF, structure see below) is a promising candidate for a so-called second-generation biofuel, which are biofuels that can be produced from residual or non-food biomass. To model the combustion of 25DMF, kinetic data for pyrolysis and oxidation reactions are needed. The pyrolysis of 25DMF is initiated by hydrogen split off from one of the methyl groups, because the corresponding bond dissociation energy is comparatively small due to resonance stabilization of the radical formed [1]. At low degrees of conversion, the subsequent bimolecular reactions H + 25DMF → products are also important.

We studied the kinetics of these two reactions in a shock tube by monitoring hydrogen atoms with resonance absorption spectrometry. In the case of the unimolecular decomposition, the formation of H atoms as reaction product was observed, whereas for the bimolecular reaction, H atoms as a reactant were detected, which were produced from fast pyrolysis of ethyl iodide in an excess of 25DMF. The temperature range was 1280-1520 K and 970-1240 K, respectively, at pressures of 1.6 and 4.7 bar with argon as bath gas.

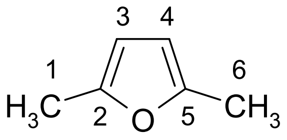
For the unimolecular decomposition, we found rate coefficients, which were pressure and temperature dependent. For the bimolecular reaction, no discernible pressure dependence could be detected, and the temperature dependence is weak [2]. The results for both reactions were analyzed in terms of statistical rate theory with molecular and transition state data from quantum chemical calculations. Master equations were used with specific rate coefficients from RRKM theory and a simplified statistical adiabatic channel model. The agreement between the measured and calculated rate coefficients is very good, which indicates the adequacy of the proposed mechanisms and the reliability of the quantum chemical results. For the H + 25DMF reaction, H atom addition to the carbon atom 2 or 5 with subsequent CH_3 split off from the intermediate radical was identified as the dominating reaction pathway [2].

We additionally performed shock tube studies with time-of-flight mass spectrometry to examine the overall pyrolysis mechanism. We were able to monitor concentration-time profiles for 25DMF, furan, and C_2H_n ($n = 2, 4, 6$). The results are discussed in terms of a mechanism proposed earlier by Lifshitz et al. [3] and more recent modifications.

T
H
U
R
S
D
A
Y

References

(1) Simmie, J.M.; Curran, H.J. *J. Phys. Chem. A* **2009**, 113, 5128-5137.
(2) Friese, P.; Simmie, J.M.; Olzmann, M. *Proc. Combust. Inst.* (submitted).
(3) Lifshitz, A.; Tamburu, C.; Shashua, R. *J. Phys. Chem. A* **1998**, 102, 10655-10670.



Structure of 2,5-dimethylfuran.

New Insights into the Atmospheric Degradation of Isoprene and Some of its Oxidation Products

Geoffrey S. Tyndall

Atmospheric Chemistry Division, NCAR Earth Systems Laboratory, National Center for Atmospheric Research, Boulder, CO 80307, United States

Isoprene is an important atmospheric constituent that can impact air quality through the production of both ozone and secondary organic aerosol. Despite many years of study, the exact details of isoprene oxidation still are not fully elucidated, and evidence is emerging for the direct formation of a number of minor products. Furthermore, measurements of the concentrations of free radicals (OH and HO_2) in isoprene-rich areas suggest an incomplete understanding of the free radical reaction pathways. We report laboratory measurements on the oxidation of isoprene and some of its reaction products under conditions of both high and low NOx, over a range of temperatures. Using a combination of techniques (IR spectroscopy, UV-vis Cavity Enhanced DOAS spectroscopy, and Proton Transfer Mass Spectrometry) we have measured a suite of oxygenated compounds including glyoxal, methylglyoxal, glycolaldehyde and hydroxyacetone produced from isoprene. Small but significant yields of both glyoxal and methylglyoxal were observed, in agreement with another recent study. We have also measured rate constants and product distributions of one of the hydroxy nitrates formed in isoprene oxidation. The results will be considered in terms of the overall isoprene oxidation mechanism and the potential to form SOA from isoprene.

Down Down Down: Vinyl Hydroperoxide Stabilization

Neil M. Donahue[1*] and Theo Kurtén[2]

[1] Carnegie Mellon University, PA, USA
[2] University of Helsinki, Finland
* Corresponding author: nmd@andrew.cmu.edu

With growing interest in the chemistry of Stabilized Criegee Intermediates (SCI) in Earth's atmosphere, we require increasingly accurate knowledge of the stabilization dynamics of ozonolysis products. A challenge to this understanding is the succession of weakly bound wells following the highly exothermic ozone alkene reaction. Based on conflicting data on the pressure dependence of stabilization reactions, we have hypothesized that stabilization into more than one well is important, including the SCI but also the subsequent vinyl hydroperoxide (VHP). High-level multireference computational calculations confirm that the VHP does indeed have a relatively tight dissociation transition state and thus is potentially vulnerable to stabilization. However, the calculations also reveal a stable complex following this transition state corresponding to a strong hydrogen-bonded complex between the products. This lowers the transition-state energy and thus confounds stabilization, at least for VHP with low carbon numbers. In order to constrain the chemistry of this complex reaction, we have performed master-equation calculations on a sequence of SCI-VHP systems, using the high-level multireference calculations for the two-carbon base system as our guide but progressively increasing the carbon number to probe the effect of increasing degrees of freedom on the stabilization behavior. The results reveal that stabilized VHP may well be important in the atmosphere, but that the overall ozonolysis potential energy surface still hides some mysteries.

Reaction kinetics of Ca, Mg and Fe atoms with $O_2(a^1\Delta_g)$

John Plane,[1*] Charlotte Whalley,[1] Laura Soriano,[1] Andrew Goddard,[1] David Glowacki,[2] and Al Viggiano[3]

[1] University of Leeds, Leeds, UK
[2] University of Bristol, Bristol, UK
[3] Air Force Research Laboratory, Kirtland AFB, NM, USA
* Corresponding author: j.m.c.plane@leeds.ac.uk

The first excited state of molecular oxygen, $O_2(a^1\Delta_g)$, is produced in the mesosphere-lower thermosphere (MLT) region of the earth's atmosphere by photolysis of O_3 at wavelengths shorter than 320 nm. $O_2(a)$ is comparatively long-lived in the MLT. The quenching life-time is more than 4 hours, much longer than the phosphorescence lifetime of 72 minutes for emission at 1.27 μm in the infra-red. The rate of O_3 photolysis in the MLT is $\sim 8 \times 10^{-3}$ s^{-1}, so that during daytime the steady-state ratio $[O_2(a)]/[O_3]$ is about 30. Since $O_2(a)$ contains almost 1 eV of electronic excitation compared with ground-state $O_2(X^3\Sigma_g^-)$, it has the potential to be significantly more reactive although it is not a radical species.

This paper describes the kinetics of $O_2(a)$ reacting with Ca, Mg and Fe atoms, which are produced in the MLT by meteoric ablation. A new method[1] for producing $O_2(a)$ cleanly and at significant concentrations was employed: Cl_2 was bubbled through a chilled alkaline solution of H_2O_2, forming $O_2(a)$ with a yield of between 16 and 26%. The absolute concentration of $O_2(a)$ was determined from the weak $O_2(a\text{-}X)$ emission at 1270 nm, using an InGaAs photodiode detector calibrated against a radiometric standard. The flow of $O_2(a)$ was then injected into a fast flow tube for kinetic measurements. Metal atoms were produced in the flow tube using two methods: thermal evaporation (Ca and Mg), and pulsed laser ablation of an Fe target. The metal atom concentrations at the downstream end of the tube were monitored by laser induced fluorescence. The following results were obtained:

Reaction	Bimolecular Rate Coefficient cm^3 $molecule^{-1}$ s^{-1}	Termolecular Rate Coefficient cm^6 $molecule^{-2}$ s^{-1}
$Mg + O_2(a)$	$< 2.4 \times 10^{-14}$	$(1.8 \pm 0.2) \times 10^{-30}$
$Ca + O_2(a)$	$(2.7 \pm 1.0) \times 10^{-12}$	$(2.9 \pm 0.2) \times 10^{-28}$
$Fe + O_2(a)$	$(1.1 \pm 0.1) \times 10^{-13}$	$< 2.4 \times 10^{-31}$

Surprisingly, the reactions of the three metals with $O_2(a)$ exhibit completely different behaviour, which was explained using electronic structure calculations and RRKM theory. $Ca + O_2(a)$ mostly occurs via recombination to produce $CaO_2(^1A_1)$, with a rate coefficient that is ~80 times larger than for the reaction $Ca + O_2(X)$. There is also limited switching through a conical intersection between the reactant singlet and product triplet surfaces, leading to the bimolecular products $CaO + O$. The reaction $Mg + O_2(a)$ occurs exclusively by recombination on a singlet surface, producing $MgO_2(^1A_1)$. The rate coefficient is ~4000 times larger than for the reaction $Mg + O_2(X)$. $Fe + O_2(a)$ produces $FeO + O$, although with a probability of only ~ 0.1%. There is no evidence for recombination, suggesting that this reaction proceeds mostly by near-resonant electronic energy transfer, producing $O_2(X)$ and $Fe(a^5F)$ (the lowest-lying excited state of Fe).

References

(1) Midey, A.; Dotan, I.; Viggiano, A. A. *J. Phys. Chem. A*, **2008**, 112, 3040–3045.

Kinetics of Elementary Steps in the Br-Initiated Oxidation of Alkenes Under Atmospheric Conditions

Patrick L. Laine,[1,2] Dow T. Huskey,[3,4] Yoon S. Sohn,[5]
J. Michael Nicovich,[3] Michael L. McKee,[6] and Paul H. Wine[1,3,*]

[1] School of Earth & Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA, USA
[2] Now at Department of Earth & Atmospheric Sciences, University of Houston, Houston, TX, USA
[3] School of Chemistry & Biochemistry, Georgia Institute of Technology, Atlanta, GA, USA
[4] Now at MWH Americas Inc., Atlanta, GA USA
[5] School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA, USA
[6] Department of Chemistry & Biochemistry, Auburn University, AL, USA
* Corresponding author: pw7@prism.gatech.edu

The Br-initiated oxidation of alkenes may play a significant role in the chemistry of marine tropospheric environments, particularly in polar regions during ozone depletion events. The bromoalkyl radicals formed via Br + alkene addition reactions typically have relatively weak C−Br bonds such that radical unimolecular decomposition often occurs in competition with radical + O_2 reaction under tropospheric conditions. As a result, the tropospheric rates of Br-initiated oxidations of alkenes can display complex temperature and pressure dependences. Using laser flash photolysis studies of Br kinetics in conjunction with supporting electronic structure calculations, we have investigated (for the first time in most cases) the kinetics and thermochemistry of early elementary steps in the Br-initiated oxidations of several alkenes including ethylene, tetramethyl ethylene (TME),[1] methyl vinyl ketone (MVK), 1,3-butadiene, and isoprene. Elementary steps investigated include hydrogen abstraction, formation/dissociation of bromoalkyl radicals, and formation/dissociation of bromoalkylperoxy radicals. At $T < 320$ K, hydrogen abstraction occurs at a significant rate only for the Br + TME reaction. Observed rate coefficients for Br addition to all alkenes investigated are large, approaching the gas kinetic limit for Br + TME, Br + 1,3-butadiene, and Br + isoprene (at $P = 1$ atm). C−Br bond dissociation enthalpies (298 K), extracted from temperature-dependent studies of bromoalkyl radical formation/dissociation kinetics, range from ~30 kJ mol^{-1} for CH_2CH_2Br to ~70 kJ mol^{-1} for the most stable radical formed via Br addition to isoprene. Allyl resonance stabilization results in formation of particularly strongly bound bromoalkyl radicals upon addition of Br to the conjugated dienes (1,3-butadiene and isoprene). At 298 K, essentially 100% of the bromoalkyl radicals formed from Br reactions with conjugated dienes react with O_2 in competition with unimolecular decomposition. However, loss of allyl resonance stabilization upon addition of O_2 to the bromoalkyl radicals results in particularly weak C−O bonds in the peroxy radicals formed following Br addition to the conjugated dienes; at higher tropospheric temperatures as well as in competitive kinetics experiments carried out in environmental chambers at temperatures near 298 K, these peroxy radicals are likely to decompose back to bromoalkyl radical + O_2 before undergoing bimolecular reaction.

References

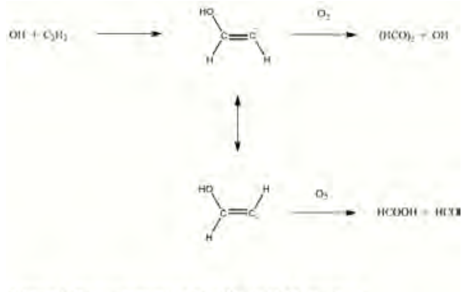
(1) Laine, P.L.; Sohn, Y.S.; Nicovich, J.M.; McKee, M.L.; Wine, P.H. *Int. J. Chem. Kinet.* **2012**, 44, 13-26.

Chemical Activation in the Product Yields of the OH/C_2H_2/O_2 system: Yields as a function of oxygen and Temperature

James Lockhart [1] Mark Blitz,[1] Dwayne Heard,[1] Michael Pilling,[1] Robin Shannon,[1]
P. Seakins,[1] David Glowacki,[2] and Struan Robertson[3]

[1] University of Leeds, UK; [2] University of Bristol, UK; [3] Accelrys, Science Park, Cambridge , UK.
Corresponding author: bmb0jpal@leeds.ac.uk

Acetylene, C_2H_2, is an important atmospheric marker for anthropogenic emissions and biomass burning. Atmospheric removal of acetylene is dominated by addition with OH. The adduct subsequently reacts with O_2 via a barrierless association reaction along two product pathways (Scheme 1).[1-3] The kinetics of the OH + C_2H_2 reaction have been studied by monitoring OH decay under pseudo-first-order conditions using both N_2 and O_2/N_2 bath gas mixtures. Experimental conditions are controlled so that the OH + C_2H_2 reaction rapidly recycles in the presence of oxygen. Monitoring OH decay in the presence, k_{O2}, and absence, k_{N2}, of O_2 allows the OH yield (Φ_{OH}) to be determined directly via $\Phi_{OH} = 1 - k_{O2}/k_{N2}$. Φ_{OH} shows no dependence on total pressure but does depend on bath gas composition (Figure 2). These observations can be rationalized as follows. OH adds to C_2H_2 to produce either a *cis* or *trans* conformer, with formation of either considered equally probable. The adducts form with ~130 kJ mol^{-1} excess energy and in N_2 become thermalized. The more stable *trans* adduct, leading to OH regeneration, is preferentially populated under thermal conditions. The dependence on f_{O2} is related to how much thermalization has occurred before the adduct has encountered O_2: high f_{O2} means reaction before the adduct is thermalized - *chemical activation* - where at the limit of pure O_2, the conformers react with O_2 where the populations are close to equal and hence Φ_{OH} ~0.5; at low f_{O2} the adduct distribution is close to thermal equilibrium, resulting in an increased Φ_{OH}. Temperature dependent Φ_{OH} have also been observed, resulting from enhanced *trans* populations as the temperature is lowered (Figure 3). In the presentation we will discuss the role of chemical activation in determining product distributions in what has mainly been considered a thermal environment, atmospheric implications, theoretical modeling of the system and the extension to higher alkynes.



Scheme 1. Product channels in the OH – C_2H_2/O_2 reaction

References
(1) Schmidt, V.; Becker, K. H. et al. *Ber. Bunsen-Ges. Phys. Chem. Chem. Phys.* **1985**, *89*, 321. (2) Hatakeyama, S.; Washida, N.; Akimoto, H. *J. Phys. Chem.* **1986**, *90*, 173. (3) Glowacki, D. R.; Pilling, M. J. *Chemphyschem* **2010**, *11*, 3836.

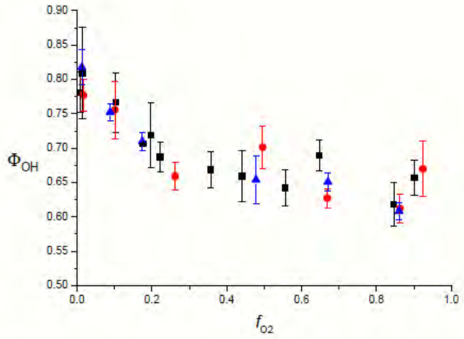


Figure 2. Variation of Φ_{OH} for the OH + C_2H_2/O_2 reaction as a function of total pressure and oxygen fraction (f_{O2}); 10 Torr (black squares), 25 Torr (red circles) and 75 Torr (blue triangles)

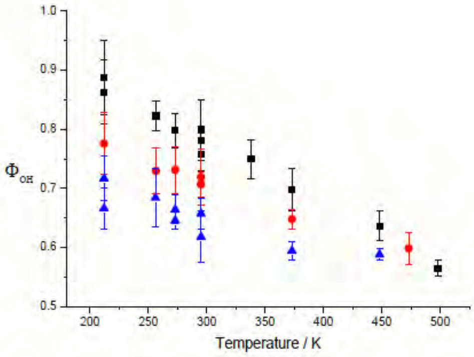


Figure 3. Temperature dependence of Φ_{OH} from 212-498 K under 10 Torr total pressure; f_{O2} = 0.01 (black squares), f_{O2} = 0.2 (red circles) and f_{O2} = 0.9 (blue triangles)

248nm photolysis of acetaldehyde: quantum yield of H and HCO and rate constant of the reaction $CH_3 + HO_2$

Pranay Morajkar, Coralie Schoemaecker and Christa Fittschen*

University Lille, Villeneuve d'Ascq, France
* Corresponding author: Christa.Fittschen@univ-lille1.fr

Acetaldehyde is an important carbonyl compounds present in the atmosphere as it is emitted to the atmosphere from plants, combustion processes etc. Its photodecomposition by sunlight generates free radicals which further influence the photochemistry of the troposphere. Recently, Moortgat et al. [1] investigated the photolysis of acetaldehyde in the wavelength range of 255 to 335 nm and provided quantum yields for the three primary photolysis processes (R1a), (R1b) and (R1c) by measuring stable end products using GC/FID.

$$CH_3\,CHO + h\nu_{248nm} \rightarrow CH_3 + HCO \qquad (R1)$$

$$\rightarrow CH_4 + CO \qquad (R2)$$

$$\rightarrow CH_3CO + H \qquad (R3)$$

Products from (R1a) and (R1c), HCO radicals and H atoms, react with O_2, but with very different rate constants:

$$HCO + O_2 \rightarrow HO_2 + CO \qquad k = 5.1 \times 10^{-12}\ cm^{-3}s^{-1}\ [2]$$

$$H + O_2\ (+M) \rightarrow HO_2 \qquad k_{30Torr} = 1.7 \times 10^{-14}\ cm^{-3}s^{-1}\ [3]$$

Therefore, measuring the time resolved HO_2 kinetics at different $[O_2]$ using laser photolysis / cw-CRDs setup provides a direct measure of the quantum yields for HCO and H atom formation from the acetaldehyde photolysis at 248 nm.

In the same system, the reaction of CH_3 with HO_2 can be studied: this reaction can play, under certain conditions (moderate temperature and high pressure), a key role in combustion processes, as HO_2 and CH_3 radicals are the dominant species in the radical pool. The reaction CH_3+ HO_2 competes with the CH_3 self recombination as the major sink for CH_3. Competition between both reactions is important as the CH_3 self recombination is a chain terminating step whereas the reaction of CH_3+HO_2 can produce new radical species such as OH and CH_3O. The only reports available in the literature concerning this reaction are theoretical calculations [4,5], to our knowledge no experimental determinations of the rate constant has been published. Both HO_2 and CH_3 radicals are formed during the photolysis of acetaldehyde, which allows determining the rate constant for CH_3 + HO_2 experimentally by modelling the time resolved decays of HO_2 radicals under different experimental conditions (photolysis energy, initial CH_3CHO and O_2 concentrations).

References

[1] Moortgat, G.K., Meyrahn, H., Warneck, P. *ChemPhysChem*. **2010**, 11, 3896 – 3908.
[2] Atkinson R. et.al. *Atmospheric Chemistry and Physics* **2006**, 6, 3625-4055.
[3] Fernandes, R. X.; Luther, K.; Troe, J.; Ushakov, V. G. *Physical Chemistry Chemical Physics* **2008**, *10*, 4313-4321.
[4] Jasper, A.W., Klippenstein, S.J., Harding, L.B. *Proc. Comb. Institute* **2009**, 32, 279–286.
[5] Zhu, R., Lin, M.C. *J. Phys. Chem. A* **2001**, 105, 6243-6248.

Radical quantum yields from formaldehyde photolysis in the 30400 – 32890 cm^{-1} (304 – 329 nm) spectral region: Detection of radical photoproducts using Pulsed Laser Photolysis-Pulsed Laser Induced Fluorescence

Cheryl Tatum Ernest, Dieter Bauer, and Anthony J. Hynes
Division of Marine and Atmospheric Chemistry, Rosenstiel School of Marine and Atmospheric Science, University of Miami, 4600 Rickenbacker Causeway, Miami, FL 33149

Formaldehyde (HCHO) is ubiquitous in the troposphere and is one of the most important carbonyl molecules in the lower atmosphere. It is produced by the oxidation of methane, isoprene, acetone, and other volatile organic compounds (VOCs), fossil fuel combustion, and biomass burning. HCHO has the potential to significantly influence both local and regional scale atmospheric chemistry and is one of the indicators of poor air quality because essentially every organic species in the atmosphere degrades with a reaction pathway that includes HCHO.

The dominant loss mechanism for HCHO is photolysis which occurs via two pathways with threshold energies indicated in parentheses:

$HCHO + h\nu \rightarrow HCO + H$ (30328.5 cm^{-1}) (R1)
$HCHO + h\nu \rightarrow H_2 + CO$ (27720 cm^{-1}) (R2)

In this work the quantum yield for the production of radical products, H+HCO has been measured directly using a Pulsed Laser Photolysis – Pulsed Laser Induced Fluorescence (PLP – PLIF) technique across the 30400 – 32890 cm^{-1} (304 – 329 nm) spectral region. This is the first study at a resolution approaching the Doppler linewidth of HCHO rotational features and also the first work to report a contiguous action spectrum across the actinic uv region. The H and HCO photofragments reacted with NO_2 and were monitored using LIF of the OH radical as a spectroscopic marker. Using the HCHO absorption cross section previously obtained in this laboratory, the relative quantum yield was determined two different ways. Direct division of the action spectrum by the absorption cross sections produced a high resolution picture of the rotationally resolved quantum yields allowing us to examine the roational dependence of the yields. These were compared with band specific yields, produced by integrating over vibrational features before division. Yields were normalized to a value of 0.69 at 31750 cm^{-1} based on the current recommendation of Sander et al. In The first high-resolution absolute radical quantum yield measurements were reported by Gorrotxategi Carbajo et al. using cavity ring down (CRD) detection of HCO with a resolution of 0.5 cm^{-1}. Absolute yields were measured at seven wavelengths and then used to scale relative yields. The resolution of the current study is estimated to be better than 0.09 cm^{-1}, a factor of five higher, and provides data over the entire spectral range whereas Gorrotxategi Carbajo et al. were unable to obtain yield measurements over several wavelength intervals due to limited signal-to-noise ratios over regions where $\sigma_{HCHO} < 1.8 \times 10^{-20}$ cm^2 molecule^{-1}. This included all of the $1_0^1 4_0^3$, $2_0^1 4_0^2 6_0^1$, and $5_0^1 + 1_0^1 4_0^1$ bands and a significant portion of the $2_0^1 5_0^1$ band. We find greater structure than prior studies and for the $5_0^1 + 1_0^1 4_0^1$ combination band centered at 31125 cm^{-1} the measured radical quantum yield is significantly less than the values reported in recent studies. The rotational and vibrational dependence of the quantum yield and its atmospheric implications will be discussed.

This work was supported by NSF

References:
Sander, S. P., et al., *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 17*, Jet Propulsion Laboratory, Pasadena, 2011.

Gorrotxategi Carbajo, P., Smith, S. C., Holloway, A. L., Smith, C. A., Pope, F. D., Shallcross, D. E. and Orr-Ewing, A. J., *J. Phys. Chem. A*, 2008, **112**, 12437-12448.

Contribution of the multigenerational oxidation process to SOA formation and ageing

Bernard Aumont[1,*], Marie Camredon[1], Richard Valorso[1], Camille Mouchel-Vallon[1], Julia Lee-Taylor[2] and Sasha Madronich[2]

[1] LISA, UMR CNRS 7583, Universités Paris Est Creteil et Paris Diderot, France
[2] National Center for Atmospheric Research (NCAR), Boulder, CO, USA

Secondary Organic Aerosols (SOA) are formed by condensation of multifunctional species produced during gaseous oxidation of Volatile Organic Compounds (VOC). The Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere (GECKO-A) has been developed to describe highly detailed gas phase oxidation schemes of organic compounds under general tropospheric conditions[1] and the partitioning of secondary organics between gas and condensed phases[2,3]. This approach leads to the development of chemical schemes involving millions of species and allows the prediction of multiphase mass budgets using first principles. GECKO-A was applied to generate highly detailed oxidation schemes for long chain organic species (C8-C24) and explore SOA formation in a box model. In this study, we examine in detail how the multi generational oxidation process contributes to SOA formation and ageing. Results will be presented showing, generation after generation, the time evolution of the volatility distribution and the oxidation degree of the organic species in the gas and aerosol phases for various hydrocarbons.

References

(1) Aumont, B; Szopa, S.; Madronich, S. *Atmospheric Chemistry and Physics*, 5, 2497-2517, 2005.
(2) Camredon, M.; Aumont, B.; Lee-Taylor, J., Madronich, S. *Atmospheric Chemistry and Physics,* 7, 5599-5610, 2007.
(3) Valorso, R. ; Aumont, B.; Camredon, M.; Raventos-Duran, T.; Mouchel-Vallon, C.; Ng, N. L.; Seinfeld, J. H.; Lee-Taylor, J.; Madronich, S. *Atmospheric Chemistry and Physics*, 11, 6895-6910, 2011

Unraveling the complexity of organic aerosol chemistry through the study of simple heterogeneous reaction systems

Paul J. Ziemann,[1*]

[1] University of California, Riverside, CA, USA
* Corresponding author: paul.ziemann@ucr.edu

The formation and processing of atmospheric organic aerosol particles involves gas phase, heterogeneous, and multiphase chemical reactions, which alter particle composition and thus affect particle chemical and physical properties such as hygroscopicity, cloud nucleating activity, and light scattering and absorption. These properties have major effects on chemical lifetimes and transport, visibility, the hydrological cycle, and climate. The mechanisms of these reactions are complex and not yet well understood. Reactions with atmospheric oxidants, primarily OH radicals, O_3, and NO_3 radicals, usually either add functional groups to molecules or cause molecular fragmentation, whereas reactions with other organic molecules form larger oligomeric species. Whereas the mechanisms of radical-initiated reactions of organic compounds have much in common, regardless of the oxidant or whether they occur in the gas phase or via heterogeneous or multiphase mechanisms, there are also differences that can significantly alter reaction kinetics and products. Elucidating these mechanism can be a challenge, because of the great complexity of many reaction systems and the large numbers of products that can be formed. Studies on reactions systems with more tightly constrained and simpler chemistry can often provide much more detailed information that can be used to understand more complex systems. In this talk I will discuss results of extensive studies we have conducted over a few years using the reaction of oleic acid aerosol particles with NO_3 radicals and N_2O_5 as a model system for radical-initiated heterogeneous/multiphase reactions. I will demonstrate that by using a diverse array of measurement techniques including mass spectrometry, nuclear magnetic resonance spectroscopy, gas and liquid chromatography, spectrophotometry (with and without compound derivatization), traditional elemental analysis, pycnometry, temperature-programmed thermal desorption, and scanning mobility particle sizing to investigate reaction kinetics and products that it is possible to develop a full chemical reaction mechanism for this system, and that the results provide interesting insights into gas phase, heterogeneous, and multiphase and chemistry.

Secondary Organic Aerosol formation in the atmosphere by new aerosol-based photo-induced processes

María Eugenia[1] Monge, Thomas Rosenørn[1], Markus Müller[1], Christian George[1], Barbara D'Anna[1], Barbara Nozière[1],Gabriella Adler[2], Yinon Rudich[2,*]

[1] Institut de Recherches sur la Catalyse et l'Environnement de Lyon, UMR 5256 CNRS/Université Lyon1, F-69629 Villeurbanne cedex, France
[2] Weizmann Institute, Rehovot 76100, Israel
[3] National Oceanic and Atmospheric Administration (NOAA), Boulder, CO, USA
* Corresponding author: Yinon.Rudich@weizmann.ac.il

The formation mechanisms of secondary organic aerosols (SOA) currently considered for in the atmosphere, mostly taking into account the gas precursor volatility, underestimate atmospheric SOA masses. Reactivity inside the aerosol particles could, in principle, account for the missing masses but the exact processes remained to be identified until now.

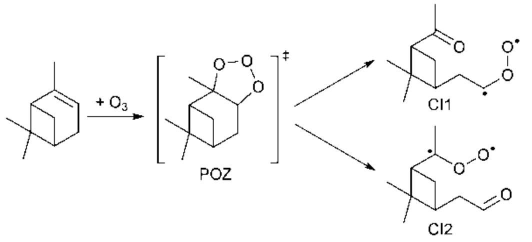
Here we report new aerosol-based photo-induced processes producing SOA at atmospheric growth rates from a range of gas precursors (isoprene, limonene, butanol, toluene…). Unlike in the current mechanisms the precursors are oxidized in the aerosol particles, not tin he gas phase, by radicals produced by the excitation of a photosentisizer present in the aerosol phase by sunlight. The resulting SOA yields are thus strongly enhanced by the reactive uptake and by the contribution of a wide range of precursors. Such photosentisizers were also identified among the multiphase reaction products of common atmospheric gases, increasing the importance of these processes in the atmosphere.

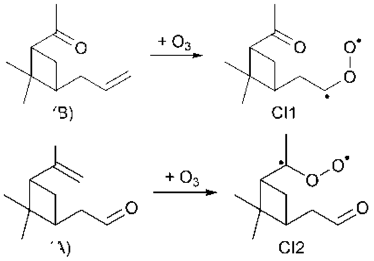
Aerosol formation from the ozonolysis of α-pinene derivatives

I. Hoare, G. Brittan, A. Russell, G. Brittan, D. Stewart, C. Pfrang and G. Marston

University of Reading, Department of Chemistry, Whiteknights, PO Box 224, RG6 6AD

The reactions of ozone with terpenes are known to be important sources of secondary organic aerosol (SOA) in the atmosphere.[2] Consequently, there have been many studies of such systems, examining the chemistry of the wide range of oxidised products the reactions generate and the size distribution the particles created. However, the mechanisms of the reactions are complex and there are many unanswered questions about the reaction mechanisms and the details of the processes leading to aerosol nucleation and growth. In previous studies,[2] we have examined the chemistry of α-pinene ozonolysis by investigating the chemistry of derivatives (enone and enal) that can lead specifically to one or other of the Criegee intermediates generated in the ozonolysis of α-pinene.



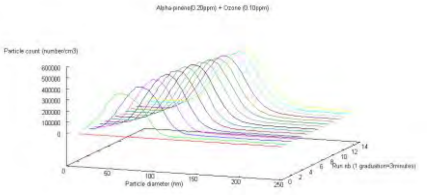


We have now extended this work by analysing the size distribution of particles generated in the reactions of ozone with α-pinene and the enone and enal derivatives using a static chamber coupled to a Scanning Mobility Particle Sizer instrument.

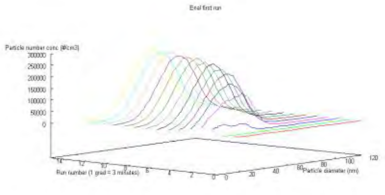
Very marked differences are observed. The aerosol generated by ozonolysis of α-pinene and the enal give qualitatively similar results, while ozonolysis of the enone gives a very much reduced yield of aerosol, as illustrated. The results are discussed in terms of previously determined underlying chemistry[2] and the implications for atmospheric chemistry.

References

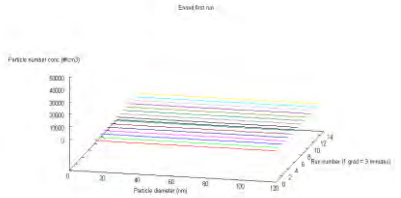
(1) Johnson, D. and Marston, G. *Chem. Soc. Rev.*, **2008**, 37, 699 – 716.
(2) Y. Ma, A.T. Russell and G. Marston *Phys. Chem. Chem. Phys.*, **2008**, 10, 4294 – 4312.



α-pinene ozonlysis



Enal ozonolysis



Enone ozonolysis

Oxidative aging of mixed component single aerosol particles

Benjamin J. Dennis-Smither,[1] Rachael E. H. Miles,[1] and Jonathan P. Reid[1,]*

[1] School of Chemistry, University of Bristol, Bristol, UK
* Corresponding author: J.P.Reid@bristol.ac.uk

Atmospheric aerosol is formed from a variety of organic and inorganic components. Heterogeneous reactions with gas phase oxidants, such as ozone, leads to the oxidative aging of atmospheric aerosol and changes in the optical properties and hygroscopicity due to changes in composition, phase, morphology and partitioning of components between gaseous and condensed phases. We present measurements of the oxidative aging of single aerosol particles trapped using optical tweezers.

Mixed component particles containing organic and inorganic components have been oxidatively aged by exposure to ozone over a range of relative humidities (RHs). Cavity Enhanced Raman Spectroscopy has been used to probe changes in particle composition, phase, morphology, volume and refractive index (RI). We have studied the oxidative aging of oleic acid (*cis*-9-octadecenoic acid; OL) and maleic acid (*cis*-butenedioic acid; MEA) by ozone in single aerosol particles formed of organic, inorganic and aqueous components.

Aerosol optical tweezers use a tightly focused laser beam to optically trap single aerosol particles within an environment in which the RH and ozone concentration experienced by the trapped particle can be controlled. We have previously used optical tweezers to probe the phase, morphology and hygroscopicity of mixed component aerosol formed of sodium chloride (NaCl) and OL.(1) In these measurements we have extended this work to investigate oxidative aging of both effloresced and deliquesced NaCl/OL particles over a range of RHs and also particles containing MEA and mixtures with inorganic and organic components.

Figure 1 shows the volume and RI of the organic phase of an effloresced mixed NaCl/OL particle during exposure to ozone and the evolving intensity of a Raman peak characteristic of OL which allows the loss of OL to be quantitatively measured. The organic volume reduces due to the formation of volatile products from the ozonolysis of OL. The timescales for the formation of these products from the reaction of OL and their partitioning into the gas phase can be compared. The formation of involatile reaction products is also observed, with greater than 50 % of the organic volume remaining involatile after oxidative aging.

Studying the oxidative aging of MEA in particles containing a variety of inorganic or organic components over a range of RHs allows us to study how changes in the host matrix, such as increasing viscosity, can affect the rates of oxidative aging and changes in particle properties.

References

(1) Dennis-Smither, B.J.; Hanford, K.L.; Kwamena, N.-O.A.; Miles R.E.H.; Reid, J.P. *J. Phys. Chem. A* **2012**, Article ASAP

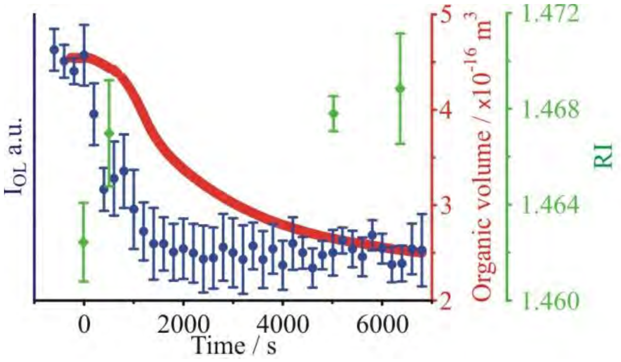


Figure 1: Temporal evolution of the intensity of Raman peak characteristic of OL (I_{OL}), volume of the organic phase, and RI of the organic phase during oxidative aging of an effloresced NaCl/OL particle. Start of ozone exposure is at t = 0 s.

Ions and Chemical Processes
Invited Friday 11:10 – 11:50

Gas Phase Ion Chemistry: From the Laboratory to the Stars

Veronica M. Bierbaum

University of Colorado, Boulder, CO, USA
veronica.bierbaum@colorado.edu

Gas phase ion chemistry is important in many environments including atmospheric, interstellar, and combustion chemistry; moreover, these processes provide insight into solution chemistry and serve as a benchmark for theory. The flowing afterglow technique,[1] developed about 50 years ago at the NOAA labs in Boulder, provides a powerful and versatile approach to the study of a wide array of ionic reactions.

This presentation will briefly review the history of the flowing afterglow technique, and the many developments that have expanded and refined the experimental capabilities. This talk will then describe how kinetics provides chemical insight into mechanisms, thermodynamics, and ionic structures for classical physical organic reactions as well as for atmospheric and interstellar chemistry.

In particular, the use of isotopes allows us to distinguish isomeric ions, reveal hidden processes, and explore reaction barriers that dictate the branching between competitive mechanisms.[2] Moreover, our gas phase studies allow an examination of the "alpha-effect," an enhanced reactivity of nucleophiles with lone electron pairs adjacent to the reactive center;[3] these studies probe whether the effect, first observed in 1962, is an intrinsic property of the nucleophile or a result of solvation.[4]

The interstellar medium is a dynamic chemical laboratory, and more than 170 neutral and ionic molecules have been detected in molecular clouds,[5] despite the harsh conditions. Our experimental studies are directed at understanding the formation and interaction of these species. Reactions of both positive and negative ions with atomic and neutral reactants will be described, and chemical networks of molecular syntheses will be presented.[6]

Future directions and instrumental developments, including Laser Induced Acoustic Desorption and Electrospray Ionization, will be discussed.

References

(1) Ferguson, E.E.; Fehsenfeld, F.C.; Dunkin, D.B.; Schmeltekopf, A.L.; Schiff, H.I. *Planet. Space Sci.* **1964**, 12, 1169–1171.

(2) Villano, S.M.; Kato, S.; Bierbaum, V.M. *J. Am. Chem. Soc.* **2006**, 128, 736-737.

(3) Edwards, J. O.; Pearson, R. G. *J. Am. Chem. Soc.* **1962**, 84, 16-24.

(4) Garver, J.M.; Gronert, S; Bierbaum, V.M. *J. Am. Chem. Soc.* **2011**, 133, 13894-13897.

(5) http://www.astrochymist.org/

(6) Snow, T.P.; V. M. Bierbaum, V.M. *Ann. Rev. Anal. Chem.* **2008**, 1, 229-259.

Rotational dependence of the proton-transfer reaction $HCl^+ + HCl \rightarrow H_2Cl^+ + Cl$

Till Uhlemann, [1] Lisa Paetow, [1] Jens Wallauer, [1] and Karl-Michael Weitzel [1,*]

[1] Philipps-Universität Marburg, Fachbereich Chemie, 35032 Marburg, Germany
* Corresponding author: weitzel@chemie.uni-marburg.de

The chemistry of gaseous ions is important for understanding a variety of processes for instance in interstellar clouds, plasma chemistry and analytical mass spectrometry. In order to understand and eventually control ion-molecule reactions, it is necessary to investigate the influence of translational and internal energy on these reactions separately. We have recently described an approach for measuring cross section for ion molecule reactions as a function of the collision energy and the internal quantum state of the ion (1,2). Here, we present a study of the rotational dependence of the proton-transfer reaction of HCl^+ in the electronic, spin-orbit and vibrational ground state with neutral HCl. State-selected HCl^+-ions with rotational quantum numbers controllable from 0 up to 10 were prepared by resonance enhanced multiphoton ionization (REMPI) (3). A guided ion beam apparatus was used to measure cross section σ as a function of the reactant ion rotational excitation and of the collision energy (1). The cross section for the title reaction decreases with increasing collision energy, as expected for exothermic reactions. For collision energies between 0.2 and 1.0 eV the cross section decreases with increasing rotational energy of the ion for rotational energy between 0 and 35 meV. For the highest rotational energies investigated the cross section increases again, indicating a change in the dynamical bottleneck. For collision energies above 1.0 eV σ becomes basically independent of the rotational quantum state of the ion. Complementary experiments utilizing deuterated hydrogen chloride (DCl) are currently under way in our laboratory. The current results for the exothermic proton transfer are compared to previous data for the reaction $HBr^+ + CO_2 \rightarrow HOCO^+ + Br$ (1,2).

References

(1) Paetow, L.; Unger, F.; Beichel, W.; Frenking, G.; Weitzel, K.-M. *J. Chem. Phys.* **2010**. 132, 174305
(2) Paetow, L.; Unger, F.; Beutel, B.; Weitzel, K.-M. *J. Chem. Phys.* **2010**, 133, 234301
(3) Michel, M.; Korolkov, M.V.; Weitzel, K.-M. *J. Phys. Chem. A* **2004**, 108, 9924-9930,

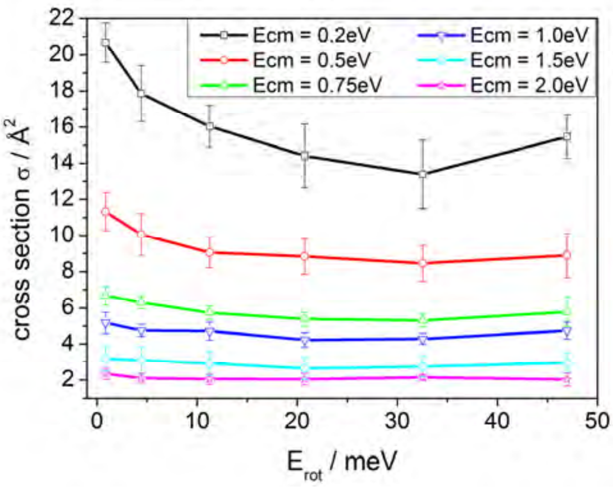


Fig. 1 Absolute cross section for the title reaction as a function of (state-selected) rotational energies at different center of mass collision energies (Ecm) as indicated.

Volatilization mechanism of 1-ethyl-3-methylimidazolium bromide ionic liquid

Ghanshyam L. Vaghjiani,[1,*] Steven D. Chambreau,[2] Jerry A. Boatz,[1]
Christine Koh,[3] Oleg Kostko,[4] Amir Golan,[4] Stephen R. Leone[3,4]

1. Propellants Branch, Propulsion Directorate, Air Force Research Laboratory, AFRL/RZSP, Edwards Air Force Base, California, 93524, U.S.A.
2. ERC, Inc., Edwards Air Force Base, California, 93524, U.S.A.
3. Departments of Chemistry and Physics, University of California, Berkeley, California, 94720, U.S.A.
4. Lawrence Berkeley National Laboratory, Berkeley, California, 94720, U.S.A.

* Email: ghanshyam.vaghjiani@edwards.af.mil; Tel: 661-275-5657; Fax: 661-275-5471

Although molten salts, more recently known as ionic liquids (ILs), have been known for almost a century (for instance, ethylammonium nitrate, mp =12 °C, was discovered in 1914),**[1]** the rapid development of ionic liquid chemistry has only occurred within the last decade. In 2000, only 217 papers were published on the subject, whereas in 2010, over 6,000 papers appeared in the literature.**[2]** The number of possible ILs has been estimated at 10^{18}.**[3]** Detailed studies of ILs offer insight into new and more complex fundamental chemistry, as well as allow for an assessment for their potential application in emerging technologies such as in solar cells, fuel electrolytes, bio- or nano-catalysts, high-energy-density propellants, and green solvents.

In order to better understand the volatilization process for ILs, the vapor evolved from heating the ionic liquid 1-ethyl-3-methylimidazolium bromide ($EMIM^+Br^-$) was analyzed via tunable vacuum ultraviolet photoionization time of flight mass spectrometry (VUV-PI-TOFMS) and thermal gravimetric analysis mass spectrometry (TGA-MS). For this ionic liquid, the experimental results indicate that vaporization takes place via the evolution of alkyl bromides and alkylimidazoles, presumably through alkyl abstraction via an S_N2 type mechanism, and that vaporization of intact ion pairs or the formation of carbenes is negligible.

Activation enthalpies for the formation of the methyl and ethyl bromides were evaluated experimentally, $\Delta H^{\ddagger}(CH_3Br) = 116.1\pm6.6$ kJ/mol and $\Delta H^{\ddagger}(CH_3CH_2Br) = 122.9\pm7.2$ kJ/mol, and the results are found to be in agreement with calculated values for the S_N2 reactions. Comparisons of product photoionization efficiency (PIE) curves with literature data are in good agreement, and *ab initio* thermodynamics calculations are presented as further evidence for the proposed thermal decomposition mechanism. Estimates for the enthalpy of vaporization of 1-ethyl-3-methylimidazolium bromide and, by comparison, 1-butyl-3-methylimidazolium bromide ($BMIM^+Br^-$) from molecular dynamics calculations and their gas phase enthalpies of formation obtained by G4 calculations yield estimates for the ionic liquids' enthalpies of formation in the liquid phase: $\Delta H_{vap}(298\ K)\ (EMIM^+Br^-) = 168\pm20$ kJ/mol, $\Delta H_{f,\ gas}(298\ K)\ (EMIM^+Br^-) = 38.4\pm10$ kJ/mol, $\Delta H_{f,\ liq}(298\ K)\ (EMIM^+Br^-) = -130\pm22$ kJ/mol, $\Delta H_{f,\ gas}(298\ K)\ (BMIM^+Br^-) = -5.6\pm10$ kJ/mol, and $\Delta H_{f,\ liq}(298\ K)\ (BMIM^+Br^-) = -180\pm20$ kJ/mol.

References

(1) Walden, P. *Bull. Acad. Sci. St. Petersburg* **1914**, 405-422.

Laboratory investigation of negative ion cold chemistry: application to Titan's upper atmosphere

Ludovic Biennier[1], Sophie Carles[1], and Jean-Claude Guillemin[2]
[1] Institut de Physique de Rennes UMR 6251 CNRS, France
[2] Sciences Chimiques de Rennes. UMR 6226 CNRS -. Ecole Nationale Supérieure de Chimie de Rennes, France

The measurements performed by the Cassini-Huygens probe in the upper atmosphere of Titan (~950 km) have revealed negatively charged molecular species over a wide range of masses (from 10 to 10 000 amu/q). The unexpected presence of large amount of anions (up to 200 ions/cm^3) means that chemical reactions and photophysics of these species have to be accounted for in the modeling of the chemistry of the atmosphere. In the work of Vuitton (1), three low mass peaks observed by the spectrometer are attributed to CN^-, C_3N^-, and C_5N^- . These nitrogen containing species could be the building blocks of the larger negative ions observed, which may be the precursors to the aerosols identified at lower altitudes. A recent modeling study suggests that the density of negatively charged aerosols could be higher than the density of the positively charged ones (2). The investigation of the negative ion chemistry is key to the modeling of Titan's atmosphere. Experimental studies of the kinetics, products and branching ratios of reactions involving these species are required to refine the production and destruction chemical pathways. In our laboratory, we have explored the reaction of CN^- with cyanoacetylene (HC_3N) over the 20-300 K temperature range in uniform supersonic flows using the CRESU technique (3). The results show that the kinetics is independent of the temperature and that C_3N^- + HCN represents the dominant exit channel. The investigation is currently extended to reactions involving larger anions such as C_3N^- .

References

(1) Vuitton, V.; Lavvas, P.; Yelle, R. V.; Galand, M.; Wellbrock, A.; Lewis, G. R.; Coates, A. J.; Wahlund, J. E. *Planetary and Space Science* **2009**, *57*, 1558-1572.
(2) Michael, M.; Tripathi, S. N.; Arya, P.; Coates, A.; Wellbrock, A.; Young, D. T. *Planetary and Space Science* **2011**, *59*, 880-885.
(3) Le Garrec, J. L.; Carles, S.; Speck, T.; Mitchell, J. B. A.; Rowe, B. R.; Ferguson, E. E. *Chemical Physics Letters* **2003**, *372*, 485-488.

Synchrotron Studies of Combustion Radical Reactions: Reaction of CH_3 Radical with Submicron Hydrocarbon Droplets

Denisia M. Popolan,[1,*] Kevin R. Wilson,[1] and Stephen R. Leone[1,2]

[1] Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA
[2] Department of Chemistry, University of California, Berkeley, CA, USA
* Corresponding author: dmpopolan@lbl.gov

Understanding the fundamental chemical processes that govern combustion phenomena offer the opportunity to optimize combustion for improved engine efficiency and minimization of pollutant formation. The elementary reactions that govern the performance of a combustion system range from direct H-atom abstraction reactions to more complex reactions involving competing addition-elimination mechanisms. In order to understand these elementary processes, less complicated model systems are required that can successfully reproduce the primary characteristics of larger molecules involved in the combustion reactions.

There is currently a growing shift away from gasoline towards less volatile fuels such as tar sands, oil shale and biofuels derived from plant matter.[1] In this context, the role of heterogeneous chemistry in the combustion process is very important since low volatility oxygenated fuels are directly injected into combustion chambers, coating cylinder walls, valves, and injectors with a liquid fuel films.

Hydrocarbon molecules such as squalane, oleic acid, linoleic acid, linolenic acid and squalene are similar in structure to the long chain alkyl (methyl, ethyl, or propyl) esters found in biodiesel fuel and represent model systems to examine the fundamental heterogeneous reactions between hydrocarbon droplets and gas phase radicals and molecules.

An atmospheric pressure flow tube reactor system composed of a droplet generation system, a flow tube reactor, and an analysis system is used in order to investigate for the first time the heterogeneous reaction of model system saturated and unsaturated hydrocarbon aerosol droplets with carbon-based radical species such as CH_3. The CH_3 radicals are created along the length of the flow tube by photolysis of CH_3I. The methyl radical reaction with hydrocarbon droplets may proceed *via* hydrogen atom abstraction or in the presence of C=C double bond *via* addition to the double bond. Preliminary results show no evidence of product formation after the reaction of CH_3 radicals with saturated hydrocarbon squalane droplets. In contrast, the reaction of CH_3 radical with the unsaturated squalene droplets reveal the appearance of new peaks at higher masses, attributed to methylated squalene. In addition, the mass spectrum shows evidence of squalene H loss. Peaks corresponding to $SqI(CH_3)_n$ (n=0–3) were also identified. In this context, detailed investigations were performed in order to understand the influence of I atoms on the reaction mechanism.

References

(1) Zador J.,Taatjes C. A. and Fernandes R. X., Prog. Energy Combust. Sci. **2011**, 37, 371-421.

Reactivity of hydroxyl radicals at air-water and air-ice interfaces

Tara F. Kahan,[1,+] R. Zhao,[1] and D. J. Donaldson[1,*]

[1] University of Toronto, Toronto, ON, Canada
[+] Currently at University of Colorado, Boulder, CO, USA
[*] Corresponding author: jdonalds@chem.utoronto.ca

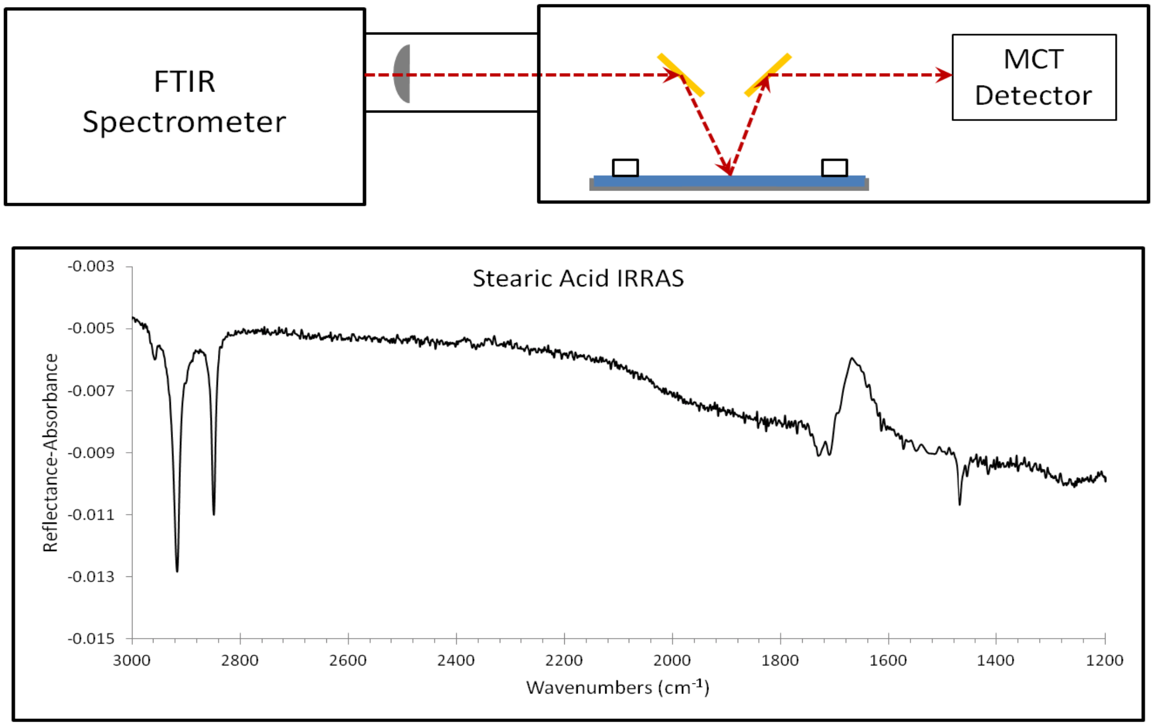
We have used a novel spectroscopic probe to monitor reaction kinetics of hydroxyl radicals (OH) *in situ* in solution and at atmospheric interfaces. We demonstrate that while hydroxyl radicals react rapidly with aromatic hydrocarbons in aqueous solution and at air-water interfaces, reactions at air-ice interfaces are immeasurably slow. Reactions between OH and aromatics are suppressed at ice surfaces whether OH is formed *in situ* at the ice surface via photolysis, or whether it adsorbs to the ice surface from the gas phase. These results may affect predictions of pollutant fate in snow and ice, as well as the composition of the overlying gas phase.

Surface catalysis at environmental interfaces: atmospheric chemistry and climate

Elizabeth C. Griffith[1] and Veronica Vaida[1*]

[1] University of Colorado, Boulder, CO, USA
* Corresponding author: vaida@colorado.edu

The water-air interface provides a unique environment for chemistry which, in turn, determines the surface composition and morphology. Understanding the processing of surface organics contributes to a better understanding of the effect atmospheric aerosols have on climate. Specifically, the experiments discussed investigate the phase (films, inclusions, micelles, etc.), phase changes, and kinetics of organics at the water-air interface. The nature of the surface of aerosols is still poorly understood, and therefore cannot be accurately represented in models. We have used the Langmuir-Blodgett trough along with Infrared Reflection-Absorption Spectroscopy (IRRAS) to study surface processing due to soluble organics in the aqueous phase in order to better understand the nature of such surfaces. The modification of the interfacial organic layer directly affects the particle's hygroscopicity, and may help to explain discrepancies in data concerning the aerosol's effect on climate.



Schematic of IRRAS set-up along with a preliminary spectrum of a floating stearic acid film

Single water molecule catalysis of hydrogen abstraction reactions

Ditte Linde Thomsen,[1,*] Theo Kurtén,[2] Solvejg Jørgensen,[1] Timothy J. Wallington,[3] Signe Bang Baggesen,[1] Cecilie Aalling[1] and Henrik G. Kjærgaard[1]
[1] Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 København Ø, Denmark
[2] Laboratory of Physical Chemistry, University of Helsinki, P.O. BOX 55, FI-00014 Finland
[3] Systems Analytics and Environmental Sciences Department, Ford Motor Company, Mail Drop RIC-2122, Dearborn, Michigan 48121-2053, USA
* Presenting author: dlt@chem.ku.dk

Atmospheric reactions have traditionally been divided into gas-phase and condensed-phase reactions. Elementary gas-phase reactions are typically assumed to involve at most two reactant molecules, with possible third bodies only playing the role of inert collision partners. Recent computational and experimental evidence has begun to modify this picture, as clustering (complexation) of reactants with molecules such as water has been shown to have a significant catalytic effect on some reaction rates (1,2).

In this work we present a computational study of the effect of a single water molecule on hydrogen abstraction by OH from small, saturated organic compounds. The hydrogen donors include amines, alcohols and fluorinated species. For molecules containing polar functional groups the transition state typically has a structure as shown on the left-hand side of Figure 1. Water molecules may stabilize the transition state by forming a ring structure as shown on the right-hand side of Figure 1. Our calculations indicate that the stabilization on the transition state electronic energy is at most a few kcal/mol. This stabilizing effect is diminished when zero point vibrational energy and entropy is included, and we predict that almost no catalytic effect should be observable at room temperature for any of the systems studied. Decreasing the temperature attenuates the entropic cost to be overcome for all compounds, and a catalytic effect might become evident below 100 K.

Since simultaneous three-body collisions in the atmosphere are extremely improbable, a necessary precondition for water catalysis is that water is already complexed with either the molecule being oxidized or with OH. Our results suggest that neither OH nor any of the studied compounds form a sufficiently strong complex with water to be significantly hydrated at temperatures and humidities encountered in the troposphere. Even though the intrinsic water catalysis for some of these reactions may be significant at lower temperatures, the net water catalysis in the atmosphere will still be minor, because the absolute water concentration and in turn the abundance of the hydrated complex decreases rapidly with decreasing temperature. In laboratory experiments, where the hydrated complexes can be generated in a jet prior to reaction, it might be possible to observe these intrinsic catalytic effects of water.

References

(1) Loerting, T. and Liedl, K. L. (2001) *J. Phys. Chem. A*. **2001**, 105, 5137-5145.
(2) Vöhringer-Martinez, E. *et al.* (2007) *Science*, **2007**, 315, 497-501.

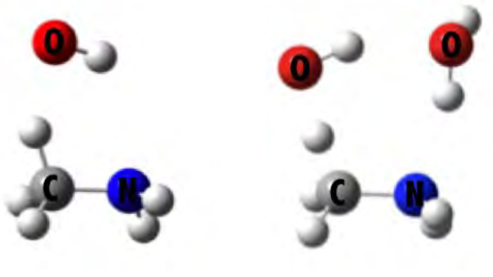


Figure 1. Transition states for the oxidation of methylamine by OH in the absence (left) and presence (right) of a water molecule.

Secondary organic aerosol formation in the atmospheric aqueous phase: Effects on product and aerosol size distributions

Barbara Ervens*

[1] CIRES, University of Colorado, Boulder, CO, USA
[2] Chemical Sciences Division, National Oceanic and Atmospheric Administration (NOAA), Boulder, CO, USA
* Corresponding author: barbara.ervens@noaa.gov

The major fraction of organic aerosol mass in the atmosphere is formed by chemical processes (secondary organic aerosol, SOA), as opposed to directly emitted organic particles (primary OA). Thus, in order to predict the mass loading and climate-relevant properties of organic aerosol that comprises a significant fraction of atmospheric particulate matter the implementation of detailed chemical mechanisms into models is necessary.

Traditional model approaches assume that SOA formation occurs by absorption of low-volatility or semivolatile oxidation products of gas phase precursors into preexisting aerosol particles. However, many recent laboratory studies have suggested that the oxidation of volatile, water-soluble compounds (e.g., small dialdehydes) in the aqueous phase of cloud droplets or deliquesced aerosol particles can lead to low-volatile products that remain in the particle phase upon water evaporation. Mechanistic studies in relatively dilute aqueous phase, which can be regarded as a proxy of cloud droplets, show the formation of keto- and dicarboxylic acids that are ubiquitous in cloud residual particles. Aqueous solutions that are more highly concentrated in terms of organic and inorganic solutes can be considered as proxies for the aqueous phase associated with aerosol particles. In such aqueous medium the preferred formation of oligomeric compounds has been observed. Such laboratory studies have resulted in the development of detailed chemical mechanisms that can be used in process models.

Results from such model studies will be presented that compare SOA mass formation in cloud droplets and aerosol particles under atmospheric conditions. Similar amounts of SOA are predicted in the two different aqueous phases even though the liquid water content of cloud droplets is about five orders of magnitude greater than that of aerosol particles. The lower solute concentrations in cloud droplets, together with the limited droplet lifetimes, can explain the similar mass production rates in clouds and aqueous aerosol particles.

Finally, differences in SOA formation in the gas and aqueous phases will be addressed. While gas phase reactions often lead to fragmentation, aqueous phase reactions favor functionalization and thus yield more highly oxidized material. Such differences in product distributions affect the SOA hygroscopicity that, in turn, impacts the interactions of aerosol particles with water vapor. Besides such chemical differences, macroscopic properties of aerosol populations are affected differently by the two SOA formation pathways: While absorption of gas phase species leads to mass addition as a function of preexisting (organic) aerosol mass, aqueous phase processes add mass to relatively larger particles that are often more hygroscopic and activated into cloud droplets. Thus, not only chemical composition and hygroscopicity but also aerosol size distributions are impacted in different ways by gas and aqueous phase SOA formation processes.

References

(1) Ervens, B.; Turpin, B. J.; Weber, R. J.; *Atmos. Chem. Phys.* **2011**, 11 11069-11102.
(2) Ervens, B.; Carlton, A. G..; Sorooshian, A.;, *in preparation.*

Henry's law coefficients and hydrolysis rate coefficients of atmospheric trace gases

Ranajit K. Talukdar,[1,2,*] Bartlomiej Witkowski, [1,2,3] A. R. Ravishankara [2], and James B. Burkholder [2]

[1] Cooperative Institute for Research in Environmental Sciences (CIRES), Boulder, CO, USA
[2] National Oceanic and Atmospheric Administration (NOAA), Boulder, CO, USA
[3] Permanent address: Department of Chemistry, University of Warsaw, Poland.
[*] Corresponding author: Ranajit.K.Talukdar@noaa.gov

Solubility coefficients of gases in liquids (Henry's law constant, H) and rate coefficients for the hydrolysis of molecules in the liquid phase (k) of atmospheric trace gases are needed to model and quantify their aqueous-phase processing. We built an experimental apparatus to measure Henry's law solubility coefficients of weakly soluble atmospherically relevant compounds and, in applicable cases, their hydrolysis rate coefficients. The apparatus, shown schematically in Fig 1, consists of a closed-cycle bubble reactor combined with a Fourier transform infrared (FTIR) spectrometer that was used to measure the gas phase concentration of the dissolving gas and products of hydrolysis reaction. Results from experiments with perfluoro-2-methyl-3-pentanone ($C_2F_5C(O)F(CF_3)_2$, PFMP) and perfluoro-2-methyl-3-butanone ($CF_3C(O)CF(CF_3)_2$, PFMB) will be presented. PFMP is currently being used as a fire suppressant in place of Halons, which have high ozone depletion potentials (ODP); PFMP and PFMB have essentially zero ODPs. The tropospheric photolysis lifetime of PFMP is relatively short, on the order of several weeks; thus, this molecule has a small Global Warming Potential (GWP). However, the hydrolysis of PFMP is known to produce HFC-227ea (CF_3CHFCF_3), a molecule that has low solubility, an atmospheric lifetime of 38.9 years, and a GWP of 3580 (100 year time horizon). Therefore, the atmospheric aqueous-phase processing of PFMP to produce HFC-227ea, even if only a minor loss pathway, can lead to a very large GWP attributable to its emission. To validate our methodology, the Henry's law solubility constants for SF_6, CF_3CHF_2 (HFC 134a), and $C_2F_5CF(CF_3)_2$ (HFC 227ea), molecules that have well established H values and extremely low hydrolysis rate coefficients, were also measured. The results of these measurements will be presented and atmospheric implications of these findings discussed.

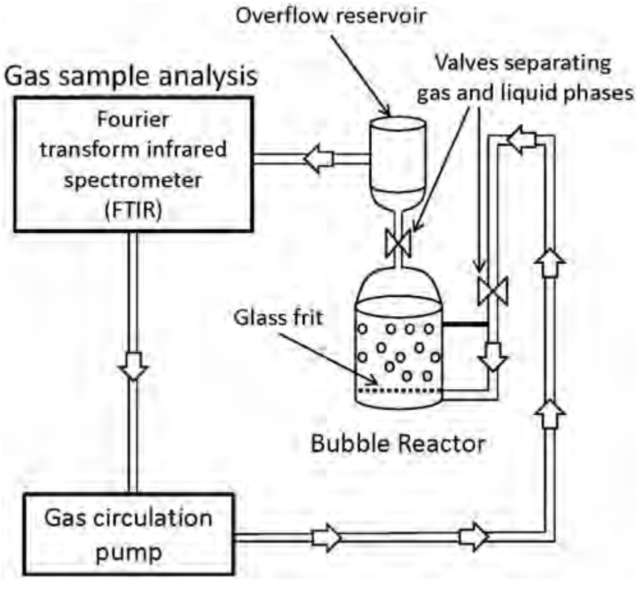


Fig. 1 Experimental setup

Aldehyde Hydration in Aqueous Solution: Estimating Activation Free Energy for Perfluoroaldehyde

Osamu Setokuchi

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan
Corresponding author: o.setokuchi@aist.go.jp

Aldehydes, formed in oxidation of VOCs, are removed mainly by photolysis and reaction with OH radicals in the atmosphere. The reaction with water molecules[1] also can play an important role in eliminating some aldehydes in gas and the condensed phase. Aldehyde hydration in media such as cloud droplets and aqueous aerosols is an important process in understanding the source of carboxylic acid in the atmosphere, since the reaction product diols can be converted into acid by reacting with OH radicals.[2] Much attention has been paid to hydration of reactive α-dicarbonyls and perfluoroaldehydes (PFAs) as the source of dicarboxylic acids found in aerosols[3] and perfluorocarboxylic acid (PFCAs) detected in rain.[4] PFAs are degradation products of fluorotelomer compounds. The experimental reaction rates for diol formation of perfluoroaldehyde, however, have not been measured in aqueous solution.

In this study, I calculated the activation Gibbs free energy ($\Delta G^{\neq}$) of hydration for some aldehydes RCHO (R=H, CH_3, CCl_3, CF_3 and C_2F_5), using a water-cluster and polarizable continuum hybrid model. I compared calculated $\Delta G^{\neq}$ s with available experimental values to estimate the rate constant for diol formation of CF_3CHO and C_2F_5CHO in aqueous solution. The geometry was optimized at the double hybrid DFT level with empirical dispersion correction. Though the water cluster models are based on the cyclic proton transfer reaction mechanism containing three water molecules proposed by Bell et al.,[5] they involve some additional micro-solvated water molecules. The increased number of water molecules leads to formation of intermediates (ion-pair complex) via a stepwise mechanism.[6] When the cluster models with seven water molecules are employed, two cluster models are produced, one with a stepwise mechanism (model A) and one with a concerted mechanism (model B), depending on the orientation of water molecules in the hydrogen-bonding network. The electron-withdrawing group favors the formation of an ion-pair complex more than the electron-donating group in model A. In model A, the bottleneck that determines the hydration rate is the transition state connecting the encounter complex and the ion-pair complex. Both Models A and B predict one to two magnitude larger rate constants for CF_3CHO and C_2F_5CHO than for CCl_3CHO.

Acknowledgements

This work was supported by JSPS Grant-in-Aid for Scientific Research 23310019.

References

(1) Vaida, V. *J. Chem. Phys.* **2011**, 135, 020901.
(2) Andersen, M. P. Sulbaek; Toft, A.; Nielsen, O. J.; Hurley, M. D.; Wallington, T. J.; Chishima, H.; Tonokura, K.; Mabury, S. A.; Martin, J. W.; Ellis, D. A. *J. Phys. Chem. A* **2006**, 110, 9854-9860. (3) Lim, Y.B.; Tan, Y.; Perri, M.J.; Seitzinger, S.P.; Turpin, B.J. *Atmos. Chem. Phys.* **2010**, 10,10521-10539. (4) Scott, B.F.; Spencer, C.; Mabury, S.A.; Muir, D.C.G. *Environ. Sci. Technol.* **2006**, 40, 7167-7174. (5) Bell, R.P.; Millington, J.P.; Pink, J.M. *Proc. R. Soc. London, Ser. A* **1968**, 303, 1. (6) Wang, B.; Cao Z. *Angew. Chem. Int. Ed.* **2011**, 50, 3266-3270.

Kinetics of the Self-Reaction of Hydroxyl Radicals

Manuvesh Sangwan[1,*], Evgeny N. Chesnokov[2], and Lev N. Krasnoperov[1]

[1] New Jersey Institute of Technology, Newark, NJ, USA.
[2] Institute of Chemical Kinetics and Combustion, Novosibrisk, Russia
* Corresponding author: ms436@njit.edu

Hydroxyl radical plays a central role both in atmospheric and in combustion chemistry. Self reaction of hydroxyl radical is very important in the laboratory kinetic studies as well as for fundamental chemical kinetics:

$$OH + OH \rightarrow H_2O + O \qquad (1a)$$
$$\rightarrow H_2O_2 \qquad (1b)$$

Channel 1b is pressure dependent, while channel 1a is assumed to be pressure independent. Despite the large number of experimental and theoretical studies of reaction 1 there is still a significant uncertainty in the rate constant of the disproportionation channel 1a. The IUPAC recommended value of $k_{1a} = 1.45\text{x}10^{-12}$ $cm^3 molecule^{-1} s^{-1}$at 298 K[1] is in significant discrepancy with the most recent measurement[2] ($2.7\text{x}10^{-12}$ $cm^3 molecule^{-1} s^{-1}$).

In this work, we determined the rate constant of channel 1a by measuring the ozone yield in the photolysis of the reactive mixture $N_2O/H_2O/O_2/He$ at 193.3 nm. Attempts to measure the rate constant of reaction 1a at low pressures (0.01 bar) were unsuccessful due to the non-stationary wall activity towards the radical decay, which was unambiguously demonstrated using the two-pulse photolysis technique. High pressure of a bath gas (1 bar, He) allowed prevention of the losses of hydroxyl radical on the walls of the reactor and avoiding complications associated with heterogeneous processes. Oxygen atoms formed in channel 1a were converted to ozone in fast reaction 3:

$$O + O_2 \rightarrow O_3 \qquad (3)$$

Transient absorption profiles of OH (308 nm) and O_3 (253 nm) were recorded at the same experimental conditions. The ozone build-up profiles were fitted using a small reaction mechanism with explicit temporal profiles of OH. Preliminary results are consistent with the low value of the rate constant of reaction 1a.

References

(1) Bedjanian, Y.; Le Bras, G.; Poulet, G. *J. Phys. Chem. A* **1999**, 103, 7017-7025.
(2) Bahng, M.-K.; Macdonald, R. G. *J. Phys. Chem. A* **2007**, 111, 3850-3861.

Kinetics of Methyl Radical Oxidation at High Pressure

Amit R. Sharma,* Lawrence B. Harding, and Stephen J. Klippenstein

Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois 60439, USA
* Corresponding author: asharma@anl.gov

High pressure experimental studies of methyl oxidation with molecular oxygen ($CH_3 + O_2 \leftrightarrows CH_3O_2$) show unusual pressure dependences, significantly different from typical falloff curves, at pressures of about 300 bar and temperatures of 300 to 400 K. Similar (unusual) pressure dependence has been observed for the rate coefficient for ozone formation in bath gas, oxidation of chlorine atom with O_2, chlorine monoxide self-reaction and in some large molecule systems. It has been proposed that the radical-complex mechanism in addition to the usual energy-transfer mechanism contributes to the total rate at such high-pressures. However, no quantitative theoretical estimation of these rates has been published.

At high-pressures, methyl radical or O_2, or both, form a van der Waals type complex with the bath-gas (R-M, radical-complex). The formation of the radical-bath gas (R-M) complex is related to the strength of the R-M bond in these complexes and at low temperatures and high bath-gas density, many of the radicals could be in the radical-complex state. The R-M radical complex further reacts with the second radical (R) to form a three-body complex. The decomposition of the $CH_3 \ldots O_2 \ldots M$ complex results in the formation of CH_3O_2 via the $CH_3 \ldots O_2$ transition state.

In this paper we present a multiple-transition state model and the formal statistical expression for estimating the kinetics of radical- radical-bath gas complex species from first principles. A high-level *ab initio* based potential energy surface is developed for $CH_3..Ar$, $CH_3..He$, $O_2..Ar$, $O_2..He$ and $CH_3..O_2$ species. The contribution due to the radical-complex mechanism is calculated based on the assumption of a two-transition state model (minimum reactive flux locations) along the reaction path describing formation of the radical-R-M complex and the dissociation of this complex.

We also explore the two-transition state model that does not involve a radical-complex intermediate. In this model the methyl radical reacts with O_2 to form a van der Waals type complex, which is then collisionally stabilized by the bath gas. Assumption of this intermediate complex leads to a two-transition state model, where the outer transition state is configurationally similar to the reactants (termed as “loose”) and the inner transition state occurring near the unimolecular product. The microcanonical and canonical rate is calculated in terms of the sum of states at the two transition states. Comparison is made with experimental data.

Acknowledgement: This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, U.S. Department of Energy, under contract number DE-AC02-06CH11357.

Investigating the Oxidation Chemistry of Ketones and Cyclic Ethers

Adam M. Scheer,[1] Subith S. Vasu,[1,2] Oliver Welz,[1] Haifeng Huang,[1] John D. Savee,[1] David L. Osborn,[1] Connie W. Gao,[3] Joshua W. Allen,[3] William H. Green,[3] and Craig A. Taatjes[1*]

[1]Combustion Research Facility, Sandia National Laboratories, MS 9055, Livermore, CA 94551 USA
[2]Department of Mechanical, Materials and Aerospace Engineering, University of Central Florida, P.O. Box 162450, Orlando, FL 32816 USA
[3]Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139 USA
* Corresponding author: cataatj@sandia.gov

Several classes of endophytic fungi convert cellulose directly into a range of molecules that are potentially useful for combustion fuels. Among the native products of these fungi are significant amounts of ketones and other oxygenates for which the ignition chemistry is not well understood. In this study, the oxidation chemistry of several ketones (diisopropyl ketone, $[(CH_3)_2CH]_2C{=}O$; isopropyl-*tert*-butyl ketone, $(CH_3)_2CHC{=}OC(CH_3)_3$; di-tert-butyl ketone, $[(CH_3)_3C]_2C{=}O$; cyclopentanone, c-$C_5H_8{=}O$; and 2-methylcyclopentanone, CH_3-c-$C_5H_7{=}O$) and cyclic ethers (tetrahydrofuran, 2-methyltetrahydrofuran, tetrahydropyran, and 1,8-cineole) has been studied, employing the technique of chlorine-initiated oxidation to examine the initial reactions that are important in autoignition of these fuels. Products of pulsed-laser initiated oxidation are monitored as a function of reaction time, mass, and photoionization energy by using Multiplexed Photoionization Mass Spectrometry (MPIMS) with tunable ionizing radiation provided by the Chemical Dynamics Beamline at the Advanced Light Source. Complementing the MPIMS experiments, direct, time-resolved detection of OH and HO_2 radicals from the Cl-initiated oxidation is performed in a slow-flow Herriott reactor cell. Quantitative OH and HO_2 species profiles provide an important monitor of the overall balance between chain-propagating and chain-branching channels, represented by OH formation, and the effectively chain-terminating formation of HO_2. The observed differences in the initial oxidation reactions displayed by these ketones and cyclic ethers will affect their autoignition properties.

The correlation of initial oxidation behavior with molecular structures is being employed to validate more general rate rules for oxidation of ketones and cyclic ethers, in the context of the Reaction Mechanism Generation program developed by the Green group at MIT. The MIT Reaction Mechanism Generator provides an important bridge between the direct observation of individual reactions in a limited temperature and pressure range and the extensive chemistry of an engine. This collaboration is aimed at developing full models to predict the potential of fungi-generated renewable fuels.

This work is supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy (USDOE)'s National Nuclear Security Administration under contract DEAC04-94AL85000. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division, of the USDOE, under contract DE-AC02-05CH11231 between Lawrence Berkeley National Laboratory and the USDOE.

High temperature study of the reaction between CN and hydrocarbons using a novel high enthalpy flow tube

Saidani.Ghassen[1,*],Biennier.Ludovic[1],Georges.Robert[1],Hugo.Edouard[1],
Gardez.Aline[1], J.B.Mitchell[1], Reddy.K.P.J[2], Arunan.E[3]

[1] Institut de Physique de Rennes UMR 6251 CNRS
[2] Indian Institute of Science, Aerospace Engineering
[3] Indian Institute of Science, Inorganic and Physical Chemistry Department
* Corresponding author: saidanighassen@gmail.com

The gas phase chemistry of CN radical is important in a variety of environments, ranging from astrophysics [1, 2] to NO_x formation and destruction in combustion [3]. For instance, neutral-neutral reactions of the CN radical with saturated and unsaturated hydrocarbons could be a dominant route in the generation of HCN which is an important precursor in the formation of NO. However, in spite of this importance, direct measurements of the rate constants of this species, particularly at high temperatures, are limited and, thus, deserve detailed laboratory investigation. The approach we have developed aims to bridge the temperature gap between resistively heated flow tubes [4, 5] and shock tubes [6, 7]. The present kinetic measurements are obtained using a new reactor combining a high enthalpy source with a flow tube and a pulsed laser photolysis–laser induced fluorescence (PLP-LIF) system to probe the undergoing chemical reactions. The high enthalpy flow tube has been used to measure the rate constant of the CN radical reaction with saturated and unsaturated hydrocarbons including ethane (C_2H_6) and ethylene (C_2H_4) over a temperature range extending from 300 to 1200 K. The majority of the reactions studied are rapid, with rate coefficients greater than 10^{-10}cm^3 molecule^{-1} s^{-1} which fit well the precedent experimental data [8-12] and confirm the theoretical suppositions [13].

The rotational temperature of the gas is also derived from the analysis of the LIF spectrum of CN radical using a Boltzmann plot. This procedure is systematically used to extract the rotational temperature of the gas flow for applied heating currents from 0 to 130 A. This work is concluded with an empirical estimation of the vibrational relaxation time of the excited CN radicals in their ground states to confirm the observation of two weak bonds assigned to the hot band transition.

Kinetics of H atom attack on unsaturated hydrocarbons using spectral uncertainty propagation and minimization techniques

David A. Sheen*, Claudette M. Rosado-Reyes, Jeffrey A. Manion, and Wing Tsang

National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

Unsaturated hydrocarbons are an important component of hydrocarbon fuels and intermediates in their oxidation. Under rich conditions, H atom attack is one of the principle pathways of the decomposition of these unsaturated compounds. Consequently, it is critical to understand the H atom attack mechanisms as part of chemical model development. Previous studies have examined the kinetics of H atom attack on various unsaturated hydrocarbons in single pulse shock-tubes. These studies have noted that there are multiple pathways by which H atom attack can proceed, so it is straightforward to measure relative rates but absolute rates are more difficult to estimate. In addition, there is a confounding influence from secondary chemistry. A multiparameter optimization and uncertainty minimization technique [1] is used to constrain a chemical model for the oxidation of $H_2/CO/C_1$-C_4 hydrocarbons against a range of measurements of the H atom attack process on toluene [2], trimethylbenzene (TMB) [3], propyne [4], and propene [5]. The recommended rate constant expressions, with 2σ uncertainties, are as follows:

$k(CH_4+H\leftrightarrow CH_3+H_2) = 10^{8.82\pm0.21}\ s^{-1}\ cm^3\ mol^{-1}\ K^{-1.6}\ T^{1.6}\exp(-5400\pm500\ K/T)$

$k(C_2H_2+CH_3\leftrightarrow p\text{-}C_3H_4+H) = 10^{11.40\pm0.18}\ s^{-1}\ cm^3\ mol^{-1}\ K^{-0.6}\ T^{0.6}\exp(-7200\pm400\ K/T)$

$k(p\text{-}C_3H_4+H\leftrightarrow a\text{-}C_3H_4+H) = 10^{18.29\pm0.21}\ s^{-1}\ cm^3\ mol^{-1}\ K\ T^{-1}\exp(-6100\pm500\ K/T)$

$k(C_3H_6+H\leftrightarrow C_2H_4+CH_3) = 10^{24.52\pm0.20}\ s^{-1}\ cm^3\ mol^{-1}\ K^3\ T^{-3}\exp(-7400\pm700\ K/T)$

$k(C_3H_6+H\leftrightarrow a\text{-}C_3H_5+H_2) = 10^{5.24\pm0.19}\ s^{-1}\ cm^3\ mol^{-1}\ K^{-2.5}\ T^{2.5}\exp(-1300\pm200\ K/T)$

$k(C_6H_5CH_3+H\leftrightarrow C_6H_6+CH_3) = 10^{6.29\pm0.19}\ s^{-1}\ cm^3\ mol^{-1}\ K^{-2.2}\ T^{2.2}\exp(-2000\pm400\ K/T)$

$k(C_6H_5CH_3+H\leftrightarrow C_6H_5CH_2+H_2) = 10^{14.10\pm0.25}\ s^{-1}\ cm^3\ mol^{-1}\exp(-4500\pm500\ K/T)$

$k(TMB+H\leftrightarrow m\text{-xylene}+CH_3) = 10^{13.83\pm0.18}\ s^{-1}\ cm^3\ mol^{-1}\exp(-3900\pm400\ K/T)$

$k(TMB+H\leftrightarrow (CH_3)_2CH_2C_6H_3+H_2) = 10^{4.57\pm0.25}\ s^{-1}\ cm^3\ mol^{-1}\exp(-4300\pm600\ K/T)$

In addition, we quantify the effect of secondary chemistry on these rate estimates and the contribution to their uncertainty. Furthermore, we demonstrate how the detailed measurements constrain the model's predictions of global properties such as ignition delay time in propene oxidation.

References

1. D. A. Sheen, H. Wang, Combust. Flame 158 (2011), 2358-2374.
2. D. Robaugh, W. Tsang, J. Phys. Chem 90 (1986), 4159-4163.
3. W. Tsang, J. P. Cui, J. A. Walker, International Symposium on Shock Waves and Shock Tubes 17 (1989), 63-73.
4. C. M. Rosado-Reyes, J. A. Manion, W. Tsang, J. Phys. Chem. A 114 (2010), 5710-5717.
5. C. Rosado-Reyes, J. Manion, W. Tsang, J. Phys. Chem. A 115 (2011), 2727-2734.

Predictive Theory for the Addition Kinetics of $^1CH_2$ with Unsaturated Hydrocarbons

Daniela Polino[1,2,*], Yuri Georgievskii[2] and Stephen J. Klippenstein [2]

[1] Politecnico di Milano, Milan, MI, Italy
[2] Argonne National Laboratory (ANL), Argonne, IL, USA
* Corresponding author: daniela.polino@chem.polimi.it

The combination of methylene with unsaturated species is an important class of reactions that can lead to the growth of aromatic compounds, a crucial issue in combustion chemistry. For example, propargyl radical (C_3H_3) is thought to be an important precursor for the formation of aromatic and soot compounds (Leung and Lindstedt 1995)[1] and one of the main routes to propargyl formation is the reaction of the first excited state of methylene, $^1CH_2$, with acetylene. Similarly, the addition of singlet methylene to ethylene yields allyl radical, which has also been postulated to be important in the formation of the first aromatic ring. Meanwhile, its addition to benzene yields toluene and/or benzyl radical, which may be a key step in the expansion from the first to the second aromatic ring. In this work we apply the direct variable reaction coordinate transition state theory (VRC-TST) approach to the quantitative prediction of the addition kinetics for these three reactions. We employ direct evaluations of the orientation dependent interaction energies at the CASPT2/cc-pVDZ level, with the CAS space consisting of two orbitals and two electrons. One dimensional corrections to these interaction energies are obtained from geometry relaxation calculations and CCSD(T)/CBS evaluations. For the $^1CH_2 + C_2H_2$ reaction the rate coefficient been measured by several authors at room temperature (Canosa-Mas et al.[2], Hack et al.[3], Hayes et al.[4], Adamson et al.[5]), while only Blitz et al.[6] and Gannon et al.[7] have made more comprehensive temperature dependent kinetic analyses (205-773 K). Prior theoretical studies of this particular reaction carried out by Guadagnini et al.[8], and by Yu and Muckerman[9], fail to reproduce the observed temperature dependence. In contrast, the corrected direct CASPT2/cc-pvdz VRC-TST approach provides quantitatively accurate predictions for the rate constant of the $^1CH_2 + C_2H_2$ combination reaction and reproduces the negative temperature dependence found in the experimental works of Blitz et al.[6] and Gannon et al.[7]. The extension to the reactions with ethylene and benzene yield important new data for combustion modelers.

References

(1) Leung, K.M.; Lindstedt, R.P. *Combust. Flame* **1995**, 102, 129.
(2) Canosa-Mas, C.E., Frey, H.M.; Walsh, R. *J. Chem. Soc. Fraday Trans. 2* **1985**, 81**,** 283-300**.**
(3) Hack, W.; Koch, M.; Wagner, H.G.; Wilms, A. *Ber. Bunsen-Ges. Phys. Chem. Chem. Phys.* **1988**, 92, 674
(4) Hayes, F.; Gutsche, G.J.; Lawrance, W.D.; Staker, W.S.; King, K.D. *Combust. Flame* **1995**, 100, 653.
(5) Adamson, J.D.; Morter, C.L.; DeSain, J.D.; Glass, G.P.; Curl, R.F. *J. Phys. Chem.* **1996**, 100, 2125-2128
(6) Blitz, M.A.; Beasley, M.S.; Pilling, M.J.; Robertson, S.H. *Phys. Chem. Chem. Phys.* **2000**, 2, 805-812.
(7) Gannon, K.L.; Blitz, M.A.; Liang, C.H.; Pilling, M.J.; Seakins, P.W.; Glowacki, D.R. *J. Phys. Chem. A* **2010**, 114, 9413-9424
(8) Guadagnini, R; Schatz, G.C.; Walch, S.P. *J. Phys. Chem. A* **1998**, 102, 5857-5866
(9) Yu, H.-G.; Muckerman, J.T. *J. Phys. Chem. A* **2005**, 109, 1890-1896

The work at Argonne National Lab was supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, under Contract No. DE-AC02-06CH11357.

Reactions of Methyl Radicals with (*Z*)-2-Butene near 1000 K

Jeffrey A. Manion,* and Iftikhar Awan,

[1] National Institute of Standards and Technology, Gaithersburg, Maryland, 20899-8320, USA
* Corresponding author: jeffrey.manion@nist.gov

Methyl radicals are important intermediates in the combustion of hydrocarbon fuels and there are few kinetic studies of their reactions at higher temperatures. The single pulse shock tube technique has been used to study the hydrogen abstraction reactions of methyl radicals with (*Z*)-2-butene at temperatures of (873 to 1031) K and pressures in the range of (1.5 to 2.2) bar with argon as the bath gas. Thermal decomposition of *tert*-butyl peroxide was used as the source of methyl radicals in the system. Products were analyzed in post-shock analyses using dual-column gas chromatography with simultaneous flame-ionization and mass-spectrometric detection. The primary observed stable products are methane and ethane, together with smaller amounts of butadiene, propene, (*Z*)-2-pentene, (*E*)-2-pentene, and 3-methyl-1-butene. The ethane/methane ratio is sensitive primarily to the relative rates of methyl recombination and abstraction of H from (*Z*)-2-butene by methyl radicals. Absolute rate constants for the latter process have been derived on this basis. Abstraction of H from (*Z*)-2-butene occurs mainly from the allylic sites and leads to methane and but-2-en-1-yl (1-methylallyl) radicals. The ensuing decomposition and radical recombination processes of 1-methylallyl account for the other olefins observed. A detailed chemical kinetic model that quantitatively describes the product distribution has been created. An analysis of the radical recombination products shows that that recombination of methyl and 1-methylallyl radicals occurs preferentially at the terminal position, which is favored by a factor of about 1.9 near 1000 K. Our data also lead to the rate constant for ejection of H from the 1-methylallyl radical, which does not appear to have been previously reported. The present results for abstraction of H by methyl radicals are compared with literature data from studies at lower temperatures.

Kinetics Studies of the Reaction of Atomic Sulfur with Acetylene

Sean Ayling,[1] Yide Gao,[1] and Paul Marshall[1,*]

[1] University of North Texas, TX, USA
* Corresponding author: marshall@unt.edu

The reaction

$$S\ (^3P_J) + C_2H_2\ (+\ M) \rightarrow \text{products}\ (+\ M)$$

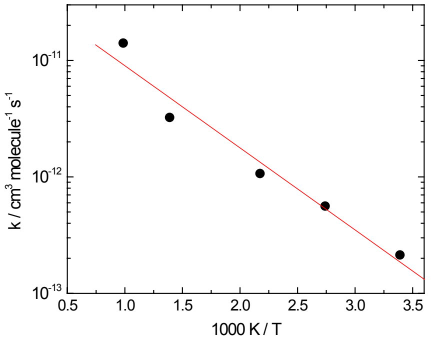
is of potential importance in a variety of applications, including combustion of sulfur-containing fuels, astrophysics and diamond deposition. Previous measurements have covered temperatures up to 484 K and do not show any pressure dependence, although a variety of potential bound intermediates are possible (1,2). The observed activation energy was well below the endothermicity for formation of, for example, HCCS + H or CCSH + H (3).

Ground-state sulfur atoms were generated by pulsed photolysis of CS_2 precursor at 193 nm, and monitored by time-resolved resonance fluorescence at 181 nm, in the presence of excess C_2H_2 in an Ar bath gas. Experiments were conducted over 295 – 1015 K and at pressures from 10 to 400 torr, and these wide ranges enabled observation of pressure-dependent kinetics. By application of Troe's formalism, the observed low-pressure limit can be expressed as $1.1 \times 10^{-30}\ T^{-5.1} \exp(-2800 / T)\ \text{cm}^6\ \text{molecule}^{-2}\ \text{s}^{-1}$ and the high-pressure limit is approximately $4.6 \times 10^{-11} \exp(-13.5\ \text{kJ mol}^{-1} / RT)\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$.

These results are discussed in terms of recently computed potential energy surfaces for singlet and triplet interactions between S and C_2H_2 (3,4), using RRKM theory and analysis of possible intersystem crossing. A singlet adduct is the most likely product.

References

(1) Little, D.J.; Donovan, R.J. *J. Photochem.* **1973**, 1, 371-377.
(2) van Roodselaar, A.; Safarik, I.; Strausz, O.P.; Gunning, H.E. *J. Amer. Chem. Soc.* **1978**, 100, 4068-4073.
(3) Leonori, F.; Petrucci, R.; Balucani, N.; Hickson, K.M.; Hamberg, M.; Geppert, W.D.; Casavecchia, P.; Rosi, M. *J. Phys. Chem. A* **2009**, 113, 4330-4339.
(4) Woon, D.E. *J. Phys. Chem. A* **2007**, 111, 11249-11253.



High-pressure-limiting rate constant for S + C_2H_2

High-pressure, low-temperature combustion chemistry: a combined experimental, theoretical, and modeling study of propane oxidation.

Leonid Sheps,[1*] Oliver Welz,[1] Judit Zádor,[1] Michael P. Burke,[2] C. Franklin Goldsmith,[3] Stephen J. Klippenstein,[2] and Craig A. Taatjes[1]

[1] Combustion Research Facility, Sandia National Laboratories, MS 9055, Livermore, CA 94551-0969, USA
[2] Chemical Sciences and Engineering Division, Argonne National Laboratories, Argonne, Illinois 60439, USA
[3] Department of Inorganic Chemistry, Fritz Haber Institute, Berlin, 14195, Germany
* Corresponding author: lsheps@sandia.gov

High-pressure combustion chemistry is an important, yet relatively underexplored area of research. Of particular interest is the pressure dependence of reaction rate coefficients and product yields that underpins the chemical reactivity of fuels and combustion intermediates in modern internal combustion engines. A key step that governs the low-temperature ($T < 800$ K) autoignition chemistry of alkanes is the reaction of alkyl radicals (R) with O_2, leading to the isomerization of the peroxy radical (RO_2) ↔ hydroperoxyalkyl radical (QOOH). The subsequent fate of QOOH depends on the competition between unimolecular decomposition and the addition of a second O_2 molecule to form OOQOOH. Whereas the unimolecular decomposition pathways are chain propagating or chain terminating, the second O_2 addition can lead to chain branching and an increased radical yield. Because QOOH needs to be stabilized by collisions for the O_2 addition to become important, this competition is pressure-dependent. Yet, much of our understanding of chemical reactivity hinges solely on low-pressure experimental data.

We will present a coupled experimental and computational study of propane oxidation over a range of conditions relevant to internal combustion engines, i.e. pressures up to 50 bar and temperatures below 800 K. 1-propyl radicals (one of the initial species formed in propane combustion) are the smallest alkyl radicals that react in significant proportion via pathways involving QOOH and the second O_2 addition. Owing to its relatively small size, the propyl + O_2 system is well-suited to accurate theoretical treatment and therefore serves as a benchmark for understanding low-T autoignition reactions. On the experimental side, we form the 1- and 2-propyl radicals by photolytically-generated Cl atom attack on propane and probe the subsequent OH radical production in an excess of O_2 by time-resolved laser-induced fluorescence. The observed OH time profiles show a complex temperature- and pressure-dependent competition of prompt (i.e., well-skipping) and slower, sequential OH formation pathways. We interpret the experimental results with the help of high-level quantum chemical calculations and RRKM-based master equation methods. The predicted rate coefficients for the individual reaction steps are incorporated into a chemical mechanism that includes the O_2 + QOOH addition and the OOQOOH decomposition pathways as well as secondary chemistry.

This work is supported by the Division of Chemical Sciences, Geosciences, and Biosciences, the Office of Basic Energy Sciences, and the U.S. Department of Energy, in part under the Argonne-Sandia Consortium on High-Pressure Combustion Chemistry, (ANL FWP # 59044; SNL FWP # 014544). Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the National Nuclear Security Administration under contract DE-AC04-94-AL85000.

Uncovering Fundamental Autoignition Chemistry: Synchrotron Photoionization Mass Spectrometry Measurements of Product Formation in Low-Temperature Isobutane Oxidation

Arkke J. Eskola*, Oliver Welz, John D. Savee, David L. Osborn, and Craig A. Taatjes

Combustion Research Facility, Sandia National Laboratories, 7011 East Ave., MS 9055, Livermore, California 94551 USA
* Corresponding author: ajeskol@sandia.gov

Product formation in laser-photolytic Cl-initiated low-temperature (550 K – 700 K) oxidation of isobutane was investigated by tunable synchrotron photoionization time-of-flight mass spectrometry in a slow-flow reactor at low pressure (4 Torr). These experiments probe the time-resolved formation of products following laser-photolytic initiation of the oxidation, and identify isomeric species by their photoionization spectra. The main oxidation products were observed at m/z = 56 (C_4H_8) and 72 (C_4H_8O), whose accompanying products are HO_2 and OH, respectively. Isobutene was the sole C_4H_8 isomer observed, whereas several isomers contribute to the C_4H_8O product spectrum. The relative yields of these oxygenated product isomers (2,2-dimethyloxirane, methylpropanal, and 3-methyloxetane) are in reasonable concord with measurements from Walker and coworkers (1) at higher temperature. Oxidation of isotopically labeled isobutane, $(CH_3)_3CD$, suggests that methylpropanal formation can proceed from both $(CH_3)_2CCH_2OOH$ and $CH_3CH(CH_2)CH_2OOH$ hydroperoxyalkyl (QOOH) isomers. Bimodal time behavior is observed for the formation of both isobutene and the C_4H_8O products; the initial prompt formation reflects "formally direct" channels, principally chemical activation, and the longer-timescale "delayed" component arises from dissociation of thermalized peroxy (ROO) and QOOH radicals. The proportion of prompt to delayed signal is smaller for the oxygenated products than for the isobutene product. This channel-specific behavior can be qualitatively understood by considering the different energetic distributions of ROO and QOOH in formally direct vs. thermal channels and the fact that higher-entropy transition states involved in the formation of oxygenated products are "tighter" than that for isobutene formation.

References

(1) Baker, R.R.; Baldwin, R.R.; Walker, R.W. *J. Chem. Soc. Faraday Trans. 1*, **1978**, 74, 2229-2251.

Acknowledgements

This work was supported as part of the Saudi Aramco "Kinetics Cluster of Excellence" under a cooperative research and development agreement (CRADA) between Sandia National Laboratories and Aramco Services Company, a U.S.-based subsidiary of Saudi Aramco, the state-owned national oil company of Saudi Arabia (CRADA SC10/01773.00, ASC Contract No. 6500007287). Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the National Nuclear Security Administration under contract DE-AC04-94-AL85000.

Quantification of hydrogen peroxide during the low-temperature oxidation of n-butane

C. Bahrini[1], O. Herbinet[1], P.A. Glaude[1]*, C. Schoemaecker[2], C. Fittschen[2] and F. Battin-Leclerc[1]

[1] Laboratoire Réactions et Génie des Procédés, CNRS, Université de Lorraine, Nancy, France
[2] PhysicoChimie des Processus de Combustion et de l'Atmosphère, Université Lille 1, Villeneuve d'Ascq, France
* Corresponding author: pierre-alexandre.glaude@univ-lorraine.fr

A significant reduction of the emissions of greenhouse gases could be achieve through an increase of the efficiency of internal combustion engines. Advanced combustion concepts that rely on compression self-ignition, as well as the improvement of safety in oxidation processes, demand an improved understanding of the detailed mechanisms of organic compounds chemical kinetics, particularly in the low-temperature oxidation regime. Hydrogen peroxide (H_2O_2), a key compound for the development of auto-ignition, has been quantified thanks to the development of a new system coupling a jet stirred reactor to a cell with an analysis by continuous wave cavity ring-down spectroscopy (cw-CRDS) in the near infrared, a quantification of H_2O_2 has been achieved for the first time under conditions close to those actually observed before the auto-ignition. If the UV or IR absorption of H_2O_2 has been used to follow its decomposition in shock tubes, H_2O_2 has never been quantified during the gas-phase oxidation of an organic reactant. Cavity ring-down spectroscopy (CRDS) has recently been proven to be a suitable method to analyse hydrogen peroxide which presents a well-structured absorption spectrum near 6639 cm^{-1}. CRDS has already been successfully used to investigate many reactive systems, related both to combustion or atmospheric chemistry.

A spherical quartz jet stirred reactor has been associated to a tubular glass cw-CRDS cell. The coupling between the cell and the reactor was performed by using a tubular quartz sonic probe with a hole of about 150 µm diameter at the tip. The size of the hole was adjusted in order to obtain the required pressure drop between the reactor slightly above atmospheric pressure and the cell. The pressure in the CRDS had to be kept around a few kPa for the absorption signal to be high enough. The pressure should nevertheless be low enough to minimize pressure broadening of absorption lines. The residence time of the gas mixture within the CRDS cell was estimated to about 0.3 s.

The study of the oxidation of n-butane was performed at temperatures between 600 and 925 K, with a mean residence time of 6s and for an n-butane/oxygen/argon mixture composition of 2.3/14.9/82.7 (in mol %) corresponding to a stoichiometric mixture for complete combustion reaction. CRDS analyses were carried out in the near infrared at wavelengths from 6620 – 6643 cm^{-1}. Note that n-butane has a continuum absorption under these conditions limiting its maximum usable initial mole fraction.

This work gives the first reliable quantification of hydrogen peroxides formed during the low temperature oxidation of an organic compound. This method can be used to build a database for the formation of this key compound for the development of auto-ignition for a wide range of fuels, allowing improving detailed kinetic models for the oxidation of organic compounds, especially the kinetics of the reactions involving HO_2 radicals.

This work was supported by the European Commission through the "Clean ICE" Advanced Research Grant of the European Research Council.

Rate constants for Reactions of Ethylbenzene with Hydroperoxyl Radical and Oxygen Molecule

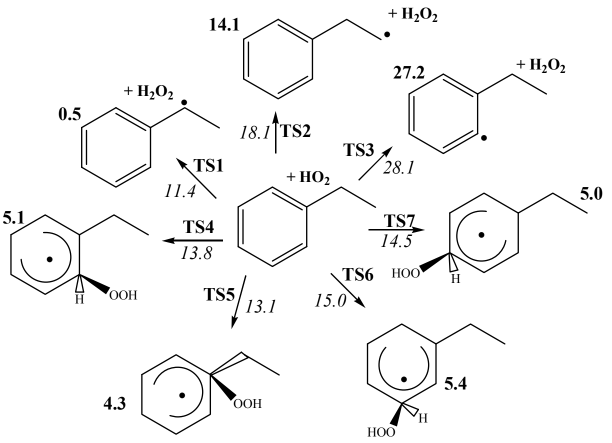
M. Altarawneh*†, B.Z. Dlugogorski, E. M. Kennedy, J.C. Mackie‡
Priority Research Centre for Energy, Faculty of Engineering & Built Environment
The University of Newcastle, Callaghan NSW 2308, Australia.

* Corresponding author: Phone: (+61) 2 4985-4286,
Email: Mohammednoor.Altarawneh@newcastle.edu.au

Reaction rate constants are commonly available for the faster elementary reactions for hydrogen atom abstractions by hydrogen atom, hydroxyl radical and oxygen atom for a wide range of hydrocarbon species. In contrast, there have been very limited experimental measurements of rate constants for the hydrogen abstraction reactions by the hydroperoxyl radical (HO_2). Hydroperoxyl radical plays a key-determining task in the autoignition region (600 – 1200 K) observed in the negative temperature coefficient (NTC) behavior [1]. It is well-documented that HO_2 plays a significant role in the reactive oxidation cycle operating at low temperatures or the so called "cool flame" reactions [2]. Alkylbenzenes in forms of xylene ($C_6H_4(CH_3)_2$) and ethylbenzene ($C_6H_5CH_2CH_3$) constitute a large portion of the total aromatic content in commercial fuels such as kerosene, gasoline and diesel, therefore, alkylbenzenes have been proposed as components for fuel surrogates [3]. Reactions of ethylbenzene with HO_2 and O_2 at low and intermediate temperatures are a major source for the formation of ethylphenyl radicals. In the current submission, reaction with ethylbenzene is addressed as a model compound for alkylbenzene. Reaction rate constants are derived for H abstraction by HO_2 from the three distinct locations of H in ethylbenzene (primary, secondary and aromatic H, with H on the ortho carbon taken as an example of unreactive aromatic H) as well as for the addition of H at the four possible sites. Rate constants are provided in the simple Arrhenius form. The dominant channel at all temperatures is found to be H abstraction from the secondary C-H bonds of the ethyl chain, whereas abstractions from the primary C-H bonds also contribute significantly at higher temperatures. Reasonable agreement was obtained with the limited literature data. Addition at the four sites of the aromatic ring and abstraction of one of the C-H aromatic bonds are rather unimportant for all temperatures. The results presented herein should be useful in modeling the lower temperature oxidation of alkylbenzenes.

References

[1] R.W. Walker. Reaction Kinetics; Ashmore, P. G., (Ed) The Chemical Society: London, 1975; Vol. 1, p 161.
[2] R.W. Walker, C. Morely, M.J Piling (Ed.), Low-Temperature Combustion and Autoignition. Elsevier, Amsterdam, 1997, p.1.
[3] J.C.G. Andrae, R.A. Head, Combust. Flame 156, (2009) 842-851.



Plausible pathways in the reaction of HO_2 with Ethylbenzene. Values in bold and italic are reaction and Activation energies respectively. All values are relative to the entrance channel.

Simple Arrhenius parameters for reactions of HO_2 with ethylbenzene fitted in the temperature range of 300-2000 K.

	A (cm^3 $molecule^{-1}$ s^{-1})	E_a/R (K)
$C_6H_5CHCH_3 + H_2O_2$	1.93×10^{-12}	6 500
$C_6H_5CH_2CH_2 + H_2O_2$	2.30×10^{-11}	10 600
$C_6H_4CH_2CH_3 + H_2O_2$	4.60×10^{-11}	16 000
o-$(HO_2)C_6H_5CH_2CH_3$	4.63×10^{-13}	8 500
ipso-$(HO_2)C_6H_5CH_2CH_3$	7.66×10^{-14}	8 000
m-$(HO_2)C_6H_5CH_2CH_3$	3.35×10^{-13}	9 000
p-$(HO_2)C_6H_5CH_2CH_3$	5.12×10^{-13}	8 800

A Detailed Kinetics Model for the Combustion of Diisopropyl Ketone

Joshua W. Allen,[1,*] Connie W. Gao[1], Subith S. Vasu[2], Stijn Vrancx[3], Ravi X. Fernandes[3], William H. Green[1], and Craig A. Taatjes[4]

[1] Deptartment of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA
[2] College of Engineering and Computer Science, University of Central Florida, Orlando, FL, USA
[3] Shock Wave Laboratory, RWTH Aachen University, Aachen, Germany
[4] Combustion Research Facility, Sandia National Laboratories, Livermore, CA, USA
* Corresponding author: jwallen@mit.edu

Recently, several classes of endophytic fungi have been identified that convert cellulosic biomass to a variety of oxygenated molecules, including several ketones and cyclic ethers, which are potentially viable as biofuels [1,2]. To evaluate the viability of these candidate biofuels, their combustion chemistry must be understood. This understanding will allow for identification of the most promising candidates, which can then become the focus of efforts to biologically engineer the production of these species. A detailed kinetics model for the combustion of novel fuels is also important for use in the development of the next generation of engines, such as the homogenous charge compression ignition (HCCI) engine.

This work presents a new detailed kinetics model for the combustion of diisopropyl ketone (2,4-dimethylpentanone), generated automatically using the Reaction Mechanism Generator (RMG) software package. RMG estimates the thermodynamic and kinetic parameters needed for detailed kinetics models by querying a database of rules and heuristics for similar species and reactions. Several new and improved rate rules have been added to the RMG database in order to improve the performance of the diisopropyl ketone model. The model has been evaluated against experimental ignition delays from our team's rapid compression machine measurements, which show a significant region of negative temperature coefficient (NTC) behavior. Autoignition chemistry is of vital importance in modeling the NTC region, particularly $R + O_2$ peroxy chemistry and pressure dependent rate coefficients. The model has also been evaluated using Multiplexed Photoionization Mass Spectrometry (MPIMS) measurements by our team.

References

(1) Singh, S. K.; Strobel, G. A.; Knighton, B.; Geary, B.; Sears, J.; Ezra, D. *Microb. Ecol.* **2011**, 61, 729–739.
(2) Strobel, G.; Singh, S. K.; Riyaz-Ul-Hassan, S.; Mitchell, A. M.; Geary, B.; Sears, J. *FEMS Microbiol. Lett.* **2011**, 320, 87–94.

Modeling syngas, formaldehyde and methanol combustion: An updated comprehensive kinetic model

S. Vranckx,[1] F.M. Haas,[2] M. Chaos,[3] F.L. Dryer,[2] and R.X. Fernandes[1,*]

[1] Physico-chemical fundamentals of Combustions, RWTH Aachen University, Germany
[2] Mechanical and Aerospace Engineering Department, Princeton University, Princeton, NJ 08544, USA
[3] FM Global, Norwood, MA 02062, USA
* Corresponding author: vranckx@swl.rwth-aachen.de

Continuing interest in syngas (CO/H_2) as a next-generation fuel has motivated recent studies on its combustion, including several kinetic models. However, several of the new experimental results, such as ignition delays, laminar burning velocities and species concentration profiles, from various experimental set-ups can not be simulated with satisfactory agreement using these existing combustion kinetic models. The goal of this work is to address these issues by updating and improving the model of Li et al. [1] for syngas and as well formaldehyde and methanol combustion (C_1 combustion).

Burke et al. [2] recently published an updated, detailed hydrogen/oxygen model, incorporating new evaluations for the thermodynamic and kinetic data and successfully tested against a wide range of validation targets. This forms a first set of updates to the C_1 model of Li et al. [1]. Secondly, more recent experimental and theoretical studies are considered for C_1 combustion such as for the sensitive reactions $OH+CO \rightarrow$ products, $CO+HO_2 \rightarrow CO_2+OH$ and $CH_3OH+HO_2 \rightarrow$ products. Simulations with the new mechanism are tested against both the original validation targets of Li et al. [1] and new validation data over a wide temperature range at higher pressures and mixtures with high amounts of H_2O or CO_2 present.

The present hierarchically-constructed, comprehensively validated C_1 model can serve both as a powerful C_1 mechanism and as a core around which to construct kinetic models for larger hydrocarbons and oxygenates.

Acknowledgements
The work on this project at the RWTH Aachen is part of the cluster of Excellence ‘Tailor Made Fuels from Biomass’ which is funded by Excellence initiative of the German federal state governments to promote science and research at German universities.

References

(1) Li, J.; Zhao, Z.; Kazakov, A.; Chaos, M.; Dryer, F.L.; Scire, J.J. *Int. J. Chem. Kinet.* **2007,** 39 (3) 109-136
(2) Burke, M.P.; Chaos, M.; Ju,Y.; Dryer, F.L.; Klippenstein, S.J. *Int. J. Chem. Kinet.* **2012**, doi:10.1002/kin.20603

Uncertainty Analysis of Chemical Thermometry and the Decomposition of Cyclohexene in a Variable Pressure Flow Reactor

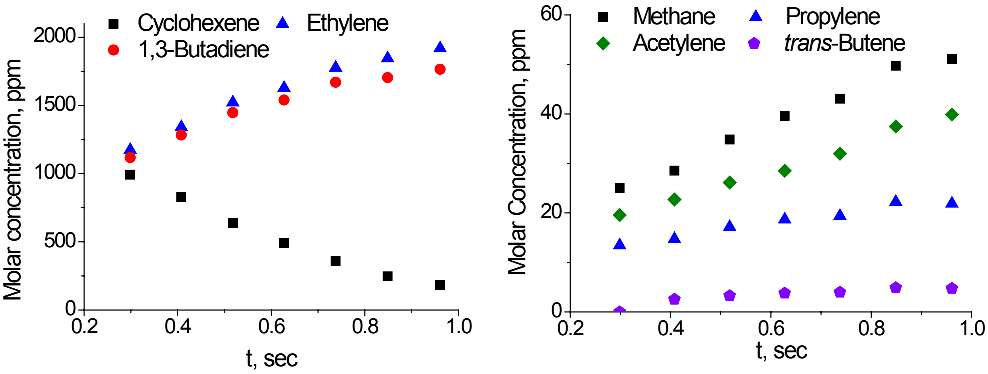
Joshua S. Heyne,[1,*] and Frederick L. Dryer[1]

[1] Princeton University, Princeton, NJ, USA
* Corresponding author: jheyne@princeton.edu

The high temperature dependence of the water elimination reaction decomposition channel for small alcohols, as with most decompositions, emphasizes the importance of accurate temperature measurements when experimentally characterizing their rate constants (1)-(2). While we have recently been studying the referenced reactions using thermocouple methods, we also considered chemical thermometry. Chemical thermometry, i.e. determining temperature by measurement of the thermal decomposition rate of a well studied compound, has been used previously by a number of authors (3,4). If the decomposition rate is well determined, the inversion of the Arrhenius expression (solving for the temperature) should yield determinations with small uncertainties. The use of chemical thermometry alleviates random errors in shock tube experiments (4) and gives a simple approach for dealing with non-idealities (3). Some authors have used this technique exclusively for the temperature determination in their experiments. Through our research, we have concluded that the uncertainty associated with chemical thermometry has not been investigated thoroughly. On the basis of literature data and new experiments that we conducted, the uncertainty analysis of two chemical thermometers: cyclohexene (reverse Diels-Alder reaction) and 1,1,1-trifloroethane (HF elimination) is reported. The work suggests that the uncertainty of chemical thermometry is far greater than expected (σ_T > 20 K). This result is consistent with new pyrolysis data for cyclohexene at 957 K and 6.1 atm in the Variable Pressure Flow Reactor, see Figure 1 and with the disparities between prior modeling studies and experimental results (5).

References

(1) Heyne, J.S.; Dooley, S.; Dryer, F. L. *ESSCI* Storrs, CT, **2011**.
(2) Heyne, J.S.; Serinyel, Z.; Dooley, S.; Dryer, F. L.; Curran, H. *CSSCI* Dayton, OH, **2012**.
(3) Tranter, R. S.; Sivaramakrishman, R.; Srinivasan, N.; Brezinsky, K. *Int. J. Chem. Kin.* **2001,** 722-731.
(4) Tsang, W.; Lifshitz, A. *Int. J. Chem. Kin.***1998**, (30), 621-627.
(5) Metcalfe, W. K.; Dooley, S.; Dryer, F. L. *Energy & Fuels* **2011**, (25) 4915-4936.



(a) **(b)**

Figure 1: Pyrolysis of cyclohexene at 6.1 atm, and 2300/997700 cyclohexene/N_2 for (a) major species and (b) minor species. The measured temperature is 957 K while chemical thermometry predicts 978 K.

Detailed Modeling of Low-Temperature Alkane Oxidation: High-Pressure Rate Rules for Alkyl + O_2 Reactions.

S.M. Villano,[1] L.K. Huynh,[1] H.-H. Carstensen,[1] and A.M. Dean[1*]

[1] Colorado School of Mines, Golden, CO, USA
* Corresponding author: amdean@mines.edu

Kinetic models are able to accurately predict the ignition behavior of a wide range of hydrocarbon fuels.[1] Such models when used in computational fluid dynamics codes provide powerful design tools to improve fuel efficiency and emissions in modern internal combustion engines and other applications. However, as engine technologies further advance and new fuels emerge, there continues to be a need for more accurate predictions over a wider range of conditions and for more diverse fuel structures and formulations. These mechanism upgrades consist of, among others, improving the accuracy of existing thermodynamic and kinetic parameters, incorporation of missing reaction pathways, and the inclusion of pressure-dependent rate coefficients to account for the wide range of operating conditions found in combustion devices.

A crucial set of reactions in hydrocarbon low-temperature oxidation is that of alkyl radicals (R) with molecular oxygen, which is responsible for chain-branching and the observed negative-temperature dependence (NTC). In this work[2,3] we employ electronic structure calculations combined with transition state theory to calculate high-pressure rate coefficients for several unimolecular channels of the alkyl peroxy radial (RO_2) and its hydroperoxy alkyl isomers (QOOH). These rate constants then serve as the basis to develop rate rules for a given reaction class. Since these reactions are pressure dependent, it is important to determine under which conditions (sets of pressures and temperatures) these high pressure rate rules are valid or when falloff effects must be accounted. Using Quantum-Rice-Ramsperger-Kassel/modified strong collision analysis we calculate apparent pressure and temperature dependent rate constants for representative reactions of small, medium, and large alkyl radicals with O_2. A comparison of concentration-time profiles obtained using either the pressure-dependent rate constants or the corresponding high-pressure values reveals that under most conditions relevant to combustion/ignition problems, the high pressure rate rules can be used directly to describe the reactions of $R + O_2$. The modeling results using the high-pressure mechanism are further examined to determine whether the reactants and intermediates equilibrate during the low temperature oxidation reactions.

References

(1) Simmie, J. M. *Progress in Energy and Combustion Science* **2003,** 29, 599-634.
(2) Villano, S.M.; Huynh, L.K.; Carstensen, H.-H.; Dean A.M. *J. Phys. Chem. A*, **2011**, 115, 13425-13442.
(3) Villano, S.M.; Huynh, L.K.; Carstensen, H.-H.; Dean A.M. *J. Phys. Chem. A*, Submitted.

A Comparative Theoretical study of the Kinetics and Dynamics of the Reaction of H Atoms with Ground-state and Excited O_2

Péter Szabó,[1] and György Lendvay[1,2]

[1] University of Pannonia, Veszprém, Hungary
[2] Institute of Materials and Environmental Chemistry, Research Center for Natural Sciences, Hungarian Academy of Sciences, Hungary
* Corresponding author: lendvay@chemres.hu

The reaction of O_2 with H atoms is one of the most important reactions in combustion. Numerous studies are available on the reaction on the lowest potential energy surface (PES) involving ground-state, triplet O_2. Recently the possibility of presence of electronically excited O_2 in flames has been proposed. While the reactivity of singlet O_2 proves to be much lower, in particular, towards saturated compounds, it can react faster with radicals than ground-state O_2. As long as excited O_2 is really present in flames, it can influence the kinetics of O-atom and OH radical formation.

We have performed quasiclassical trajectory calculations on the $O_2 + H \rightarrow O + OH$ reaction using the PESs correlating with $O_2(^3\Sigma_g^-)$ as well as with O_2 $(^1\Delta_g)$, both developed by Guo and coworkers. The excited-state reaction is exoterm by about 0.43 eV in contrast to the ground-state reaction which is 0.53 eV endoterm. There is a deep well on both PESs which corresponds to ground-state and electronically excited HO_2; this well is less deep in the excited state (2 eV below O + OH) than in the ground state (2.85 eV). In the excited state there is a potential barrier of about 0.26 eV in the entrance channel, in contrast to the barrierless entrance channel of the ground-state reaction.

According to the trajectory calculations the excitation function for the reaction starting from excited-state O_2 raises above zero at about 0.3 eV and increases almost linearly, in good agreement with the exact qunatum mechanical calculations by Guo. This reflects much larger reactivity than the ground-state cross sections having a threshold above 0.6 eV and remain much smaller than the excited-state data. For the reaction of excited O_2 the thermal rate coefficient is about 10^{-16} cm^{3}molecule^{-1}s^{-1} at room temperature and about 10^{-12} cm^{3}molecule^{-1}s^{-1} at 1500 K, the latter is two orders of magnitude larger than the respective ground-state rate value..

Comparions of the details of the dynamics will be presented.

CFD Tracing of Unburned Hydrocarbon Deposits in Combustion Chamber Walls Due to Wall Quenching of Various Gasoline Mixtures

David Rodriguez,[1] Jesus Mijares,[1] Raul Corral, [1] Naveen Ramunigari,[1] and Paul Rodriguez[1*]

[1] University of Texas at El Paso, El Paso, TX., USA
* Corresponding author: prodriguez7@miners.utep.edu

The study of unburned hydrocarbons is crucial in the optimization of internal combustion engines in order to reduce the carbon footprint. A computational fluid dynamic (CFD) model using FLUENT was used in order to trace the unburned hydrocarbons of various air-fuel gasoline mixtures. The model includes the deposition of unburned hydrocarbon deposits in the combustion chamber wall due to wall quenching of the gasoline mixture. The amount of unburned hydrocarbons was traced at the exhaust stroke stage of combustion due to the scraping of the piston to the cylinder walls.

.

References

(1) A.K. Oppenheim; *Combustion in Piston Engines*. **2004.**
(2) W.C. Gardiener; *Gas-Phase Combustion Chemistry.* **2000.**

High Temperature Kinetics of O-substitution in Ethers and Peroxides Reaction Class

Yu. V. Suleimanov[1,2*] and W. H. Green[1]

[1] Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

[2] Department of Mechanical and Aerospace Engineering, Combustion Energy Frontier Research Center, Princeton University, Princeton, New Jersey 08544
* Corresponding author: ysuleyma@mit.edu

Reliable estimates of high-pressure-limit reaction rates as a function of temperature are essential for the development of reaction sets that can be used to model complex chemical processes.
This work reports a series (more than 100) of rate coefficients computed for representative radical O-substitution reactions in ethers ($R_1OR_2+R_3 \rightarrow R_1OR_3+R_2$) and peroxides ($R_1OOR_2+R_3 \rightarrow R_1OR_3+OR_2$) up to c4. This class of reactions was previously omitted from our kinetics libraries of the Reaction Mechanism Generator software [1] due to very scanty data available in the literature [2]. Rate coefficients were calculated using transition state theory and CBS-QB3 computational chemistry calculations. The effect of hindered internal rotations was included via rotor potential energy scans and solution of the one-dimensional Schrodinger equation. This work highlights fast reactions that may be important for hydrocarbons oxidation and therefore should be taken into account in the kinetic models. The effects of branching and double and triple bonds conjugate to oxygen atom under radical attack are also analyzed.

[1] Green, W. H.; Allen, J. W.; Ashcraft, R. W.; Beran, G. J.; Class, C. A.; Gao, C.; Goldsmith, C. F.; Harper, M. R.; Jalan, A.; Magoon, G. R.; Matheu, D. M.; Merchant, S. S.; Mo, J. D.; Petway, S.; Raman, S.; Sharma, S.; Song, J.; Van Geem, K. M.; Wen, J.; West, R. H.; Wong, A.; Wong, H.–W.; Yelvington, P.E.; Yu, J. "RMG - Reaction Mechanism Generator v3.3", **2011**, http://rmg.sourceforge.net/

[2] Manion, J. A.; Huie, R. E.; Levin, R. D.; Burgess, Jr., D. R.; Orkin, V. L.; Tsang, W.; McGivern, W. S.; Hudgens, J. W.; Knyazev, V. D.; Atkinson, D. B.; Chai, E.; Tereza, A. M.; Lin, C.-Y.; Allison, T. C.; Mallard, W. G.; Westley, F.; Herron, J. T.; Hampson, R. F.; Frizzell, D. H. NIST Chemical Kinetics Database, NIST Standard Reference Database 17, Version 7.0 (WebVersion), Release 1.4.3, Data version 2008.12, National Institute of Standards and Technology, Gaithersburg, MD; http://kinetics.nist.gov/.

The Kinetics of Gas-phase Reactions of Selected Monoterpenes and Cyclo-alkenes with Ozone and Nitrate Radicals Studied by Headspace Solid-Phase Microextraction (HS-SPME)

S. Almabrok, G. Marston and C. Pfrang

Department of Chemistry, University of Reading, Reading, Berkshire, RG6 6AD, UK

Keywords: Relative rate technique, HS-SPME, Monoterpenes.

Presenting author email: s.h.almabrok@reading.ac.uk

Oxidation of volatile organic compounds in the troposphere is primarily initialised by hydroxyl radicals, ozone, and nitrate radicals,NO_3,with the dominant degradation route being determined by the relative concentrations of the oxidants as well as the rate coefficients for the reactions of the oxidised compounds with these species(1). In this study, a novel variant of the relative rate method has been employed to measure the room-temperature rate coefficients for the gas-phase reactions of ozone and NO_3 with selected monoterpenes and cycle-alkenes with structural similarities to monoterpenes. Measurements were carried out at 298± 2 K and 760 ± 10 Torr. The experimental results were obtained by combining headspace solid-phase microextraction (HS-SPME) sampling with gas chromatography-mass spectrometry (GC-MS) detection. The experimental set-up is depicted in Fig.1. Fig. 2 (a) illustrates the HS-SPME calibration for α-pinene while Fig.2 (b) gives an example of a kinetic plot used for derivation of the rate coefficients.

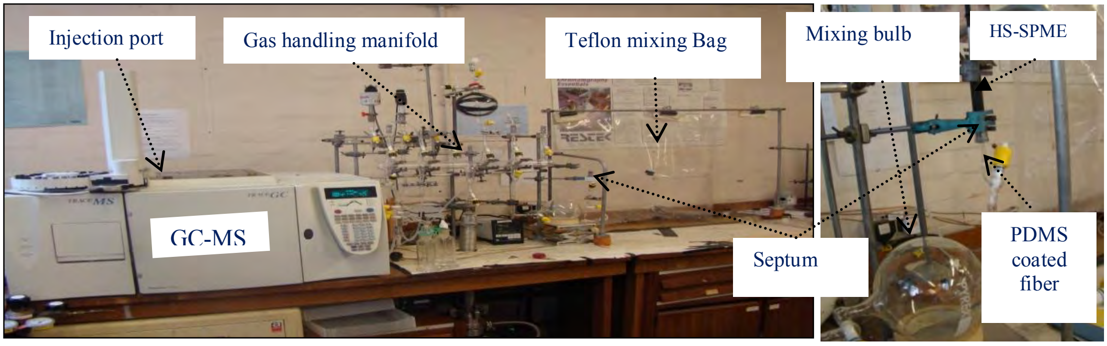


Figure.1: Experimental set up for combining HS-SPME with GC-MS analysis.

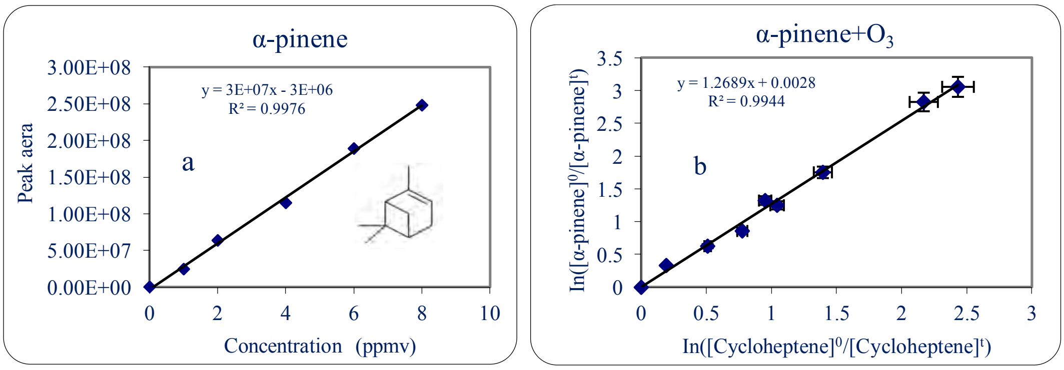


Figure 2 (a & b): (a): Calibration of α-pinene using HS-SPME and (b) Relative rate plot reacting O_3 with α-pinene vs. cyclohepten (Reference compound).

References.

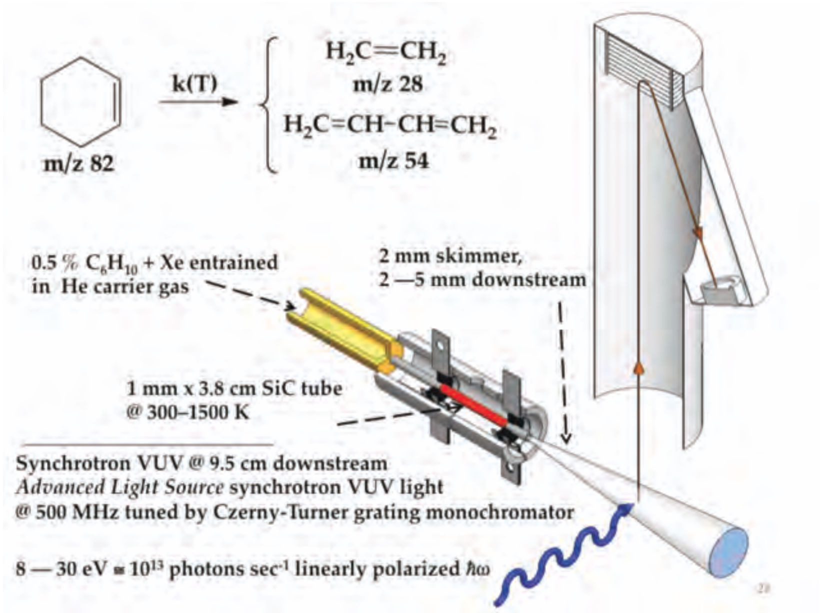
1- B.J. Finlayson-Pitts and J.N. Pitts Jr., *Chemistry of the Upper and Lower Atmosphere,* Academic Press, San Diego, 2000.

Temperature Measurement in a Microtubular Flow Reactor

Kimberly N. Urness,[1,2,*] AnGayle K. Vasiliou,[3] David L. Osborn,[4] Musahid Ahmed,[5] Amir Golan,[5] John W. Daily,[2] John F. Stanton,[6] John R. Barker,[7] and G. Barney Ellison[1]

[1] Department of Chemistry & Biochemistry, University of Colorado, Boulder, CO, USA
[2] Department of Mechanical Engineering, University of Colorado, Boulder, CO, USA
[3] Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA
[4] Combustion Research Facility, Sandia National Laboratory, Livermore, CA, USA
[5] Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA
[6] Department of Chemistry, University of Texas, Austin, TX, USA
[7] Department of Atmospheric, Oceanic & Space Sciences, University of Michigan, Ann Arbor, MI, USA
* Corresponding author: Kimberly.Urness@colorado.edu

We are developing a microtubular reactor to pyrolyze biomass samples (sugars and lignins). To characterize the thermodynamic conditions in the microtubular flow tube, we have pyrolyzed cyclohexene as a chemical thermometer.[1] The reaction kinetics of the retro-Diels-Alder fragmentation of cyclohexene to ethylene and 1,3-butadiene is well studied.[2] Cyclohexene is decomposed in a heated silicon carbide (SiC) reactor under continuous flow conditions over a range of reactor wall temperatures from 300 to 1500 K; the residence time, *t*, in the flow reactor has been estimated to be 50–200 μsec. A dilute gas mixture of 0.5% cyclohexene and xenon (as an internal standard) in helium emerges from the reactor as a skimmed molecular beam at a pressure of approximately 1 μTorr, where all reactions cease. Photoionization mass spectroscopy is used to detect cyclohexene, ethylene, and 1,3-butadiene relative to the internal standard, Xe. The cyclohexene, being in a constant temperature reactor for a known residence time, decomposes and the rate constant can be deduced. From the temperature and pressure dependence of the rate constant, the effective, chemical temperature of the microtubular reactor can be deduced. There are two problems with this simple analysis. First, the rate constant must be known with confidence. Second, the pressure and, perhaps, temperature, are not constant in the reactor. Experimental results and the analysis will be presented.



References

(1) Tranter, R.S., Sivaramakrishan, R., Srinivasan, N., Brezinsky, K. *Int. J. Chem. Kinet.* **2001**, *33*, 722-731.
(2) Kiefer, J.H., Shah, J.N. *J. Phys. Chem.* **1987**, *91,* 3024-3030.

Analysis of α-acyloxyhydroperoxy aldehydes with electrospray ionization – tandem mass spectrometry (ESI-MS^n)

Bartlomiej Witkowski* and Tomasz Gierczak

University of Warsaw, Faculty of Chemistry, al. Żwirki I Wigury 101, 02-089 Warsaw, Poland
* Corresponding author: bwitk@chem.uw.edu.pl

The investigation of chemical composition and formation mechanism of the secondary organic aerosol (SOA) formed during the gas – phase ozonolysis of α – pinene has been the subject of numerous laboratory and field studies for the last two decades. Recently, it was concluded that high – molecular weight (HMW) compounds significantly contribute to the biogenic SOA mass. It is believed that the possible pathway leading to the formation of the observed HMW compounds involves gas phase reactions of the stabilized Criegee intermediate (SCI) with the primary productsof the ozonolysis reaction[1]. It has been also proposed that the extremely low - volatile α-acyloxyhydroperoxy aldehydes formed from the reaction of the SCI with carboxylic acids can induce the particle formation by acting as the nucleation precursors during SOA formation [1,2].

Popularization of the soft – ionization technique like electrospray ionization (ESI) enables to preserve molecular integrity of those HMW SOA components. However, due to lack of the appropriate standards, and therefore well established quantification methods, the detected HMW SOA components can be only tentatively identified. Structures in the majority of the studies published up – to date are based on either the elemental formula assignment using high resolution (HR) - MS and/or tandem mass spectra interpretation. Therefore, in order to improve the current methodology, new methods for identification of HMW SOA components needs to be introduced.

Results of the analysis of the α-acyloxyhydroperoxy aldehydes using ESI-MS^n and LC/MS will be presented. Fragmentation pathways of the 13 synthesized standards were investigated by tandem mass spectrometry and confirmed using deuterated compounds. The major fragmentation pathways were found to be common for all of the α-acyloxyhydroperoxy aldehydes, therefore it was possible to predict the mass spectra of this class of compounds. As a confirmation of this conclusion, one α-acyloxyhydroperoxy aldehyde synthesized using liquid phase ozonolysis of α-pinene in the presence of cis - pinonic acid was analyzed. Very good agreement of the predicted mass spectra and the experimental data was obtained. Those results underlines the possible applications of the developed methodology for the identification of the α-acyloxyhydroperoxy aldehydes in SOA formed from during the gas – phase ozonolysis of α-pinene.

(1) Hallquist, M.; Wenger, J. C.; Baltensperger, U.; Rudich, Y.; Simpson, D.; Claeys, M.; Dommen, J.; Donahue, N. M.; George, C.; Goldstein, A. H.; Hamilton, J. F.; Herrmann, H.; Hoffmann, T.; Iinuma, Y.; Jang, M.; Jenkin, M. E.; Jimenez, J. L.; Kiendler-Scharr, A.; Maenhaut, W.; McFiggans, G.; Mentel, T. F.; Monod, A.; Prevot, A. S. H.; Seinfeld, J. H.; Surratt, J. D.; Szmigielski, R.; Wildt, J. *Atmos. Chem. Phys.* **2009**, *9*, 5155-5236.

(2) Lee, S.; Kamens, R. M. *Atmos. Environ.* **2005**, *39*, 6822-6832.

Complete decomposition of 1-chloroprpane behind the reflected Shock Waves in the temperature range of 950 - 1480K

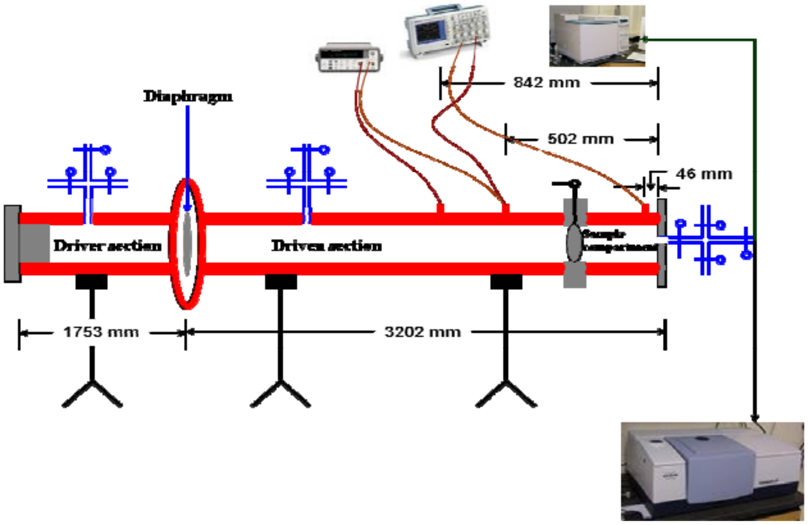
G. Sudhakar,[1] B. Rajakumar,[1,*]

[1] Indian Institute of Technology Madras, Chennai 600 036, INDIA

A Single Pulse Shock Tube (SPST) facility is built and calibrated in our research laboratory at IIT Madras to study the kinetics and thermo chemistry of various molecules of interest in combustion as well as in Earth's atmosphere. Using this facility, thermal decomposition of 1-chloropropane was investigated in the temperature range of 950 - 1480K behind the single pulse reflected shock waves. The decomposition was carried out at a relative pressure of 25 bar with a typical reaction times of 500µs. Unimolecular elimination of HCl was found to be the major decomposition channel when the temperatures are below 1150K, which was in consistent with the earlier studies[1,2]. The C-C bond dissociation becomes dominant at higher temperatures and leads to the formation of various products. While propylene, Ethylene being major products, methane, ethane and propane were observed to be minor products. The rate coefficients for the major as well as minor channels are obtained in the present study. The complete decomposition is simulated with the most appropriate reaction mechanism in the covered temperature range. In addition to the experimental studies, DFT calculations have been carried out to find the major decomposition pathways and compared with the experimental results. The complete results will be discussed in the presentation at the conference.

References

(1) Okada, K.; Tschuikow-Roux, E.; Evans, P.J. J. Phys. Chem, **1980**,84, 467 – 471.
(2) Evans, P.J.; Ichimura, T.; Tschuikow-Roux, E. Int. J. Chem. Kinet. **1978**,10, 855 - 869.



Schematic diagram of the established SPST facility at IIT Madras

A HIGH-REPETITION-RATE TIME-OF-FLIGHT MASS SPECTROMETRY STUDY OF 3-PENTANONE PYROLYSIS BEHIND REFLECTED SHOCK WAVES

M. Aghsaee*, M. Fikri, S.H. Dürrstein, C. Schulz

IVG, Institute for Combustion and Gasdynamics and CENIDE, Center for Nanointegration, University of Duisburg-Essen, 47048 Duisburg, Germany
*Corresponding author: mohammad.aghsaee@uni-due.de

Amongst other ketones (e.g., acetone) 3-pentanone has gained importance as a fluorescence tracer in combustion studies. These tracers are used to monitor quantities such as temperature, fuel concentration or equivalence ratio under practically relevant conditions or in practical combustors, respectively, using non-intrusive laser imaging techniques [1]. Ketones are frequently used as tracers because their fluorescence can be excited by common UV lasers [1]. Despite the fact that 3-pentanone can be used as a tracer in combustion studies kinetic information such as rate constants or branching ratios is very scarce. Therefore, predicting the temperature-dependent decomposition as well as the interaction of the decomposition products with the fuel is difficult. Serinyel et al. [2] published a detailed oxidation mechanism for 3-pentanone, but still there is an urgent need for validated kinetics parameters such as decomposition rate constants. Therefore, we studied the thermal decomposition of 3-pentanone in the 1085–1400 K temperature range at pressures around 1.7 bar using a shock tube coupled to a high-repetition-rate time-of-flight mass spectrometer (TOF-MS) [3]. The investigated mixtures contained 0.5 or 1.0% 3-pentanone in neon. 1% argon was used as an internal standard for the mass spectrometer. The raw mass spectra were converted to absolute concentration-time profiles by calibration as described in [4]. Concentration-time profiles both for 3-pentanone and the main products (C_2H_4 and CO) will be presented and compared to preliminary results of simulations that are based on the mechanism given in [2].

References

1 C. Schulz, V. Sick, *Progr. Energy Combust. Sci.* **2005**, 31 ,75-121.
2 Z. Serinyel, N. Chaumeix, G. Black, J. M. Simmie, H.J. Curran, *J. Phys. Chem. A* **2010**, 114, 12176-12186.
3 R. D. Kern, H. J. Singh, Q. Zhang, in: *Handbook of Shock Waves*, **2001**, Vol. 3, Chemical Reactions in Shock Waves and Detonations (Ed. A. Lifshitz), *Academic Press*, San Diego, .
4 S. H. Dürrstein, M. Aghsaee, L. Jehrig, M. Fikri, C. Schulz, *Rev. Sci. Inst.* **2011**, 82, 084103-01-07.

Atmospheric reactivity of Biofuel

S. Jørgensen,* K. B. Ørnsø, V. F. Andersen, O. J. Nielsen, M. S. Johnson

Department of Chemistry, University of Copenhagen, 2100 Copenhagen, Denmark
* Corresponding author: solvejg@chem.ku.dk

Concerns related to climate change and energy security has led to a substantial increase in the global production of biofuels over the past decade. Fatty acid methyl esters (FAMEs) made from transesterification of plant oils or animal fats are the dominant biofuel in the EU. The widespread use of FAMEs in diesel blends will lead to their release into the atmosphere. It is therefore essential to know the atmospheric impact of any potential biofuel. The main atmospheric loss process is reaction with hydroxyl (OH) radicals.

We will consider the atmospheric degradation of esters $CH_3(CH_2)_xC(O)O(CH_2)_yCH_3$ (where x=0,1,2,3 and y=0,1,2,3) which serves as model compounds for biofuel (1-4). The OH radical abstracts a hydrogen atom from the ester and often there are several sites for H-abstraction. Each H-abstraction site leads to different reaction products. It is important to know the branching ratio between the different H-abstraction channels in order to predict which biofuel compound has the least environmental impact. There is a great interest in discovering the underlying factors causing these unexpected reactivities, which is likely to involve reactant and product complexes.

In this presentation we will study the hydrogen abstraction reaction mechanism between esters and OH radical using electronic structure theory. We will estimate the branching ratio of different reaction channels.

For example for methyl acetate $CH_3C(O)OCH_3$, the probability that the OH radical abstracts a hydrogen atom of the $–OCH_3$ group is predicted to be greater than 90 % (1-2). This reaction channel dominates since both the structures of the reactant complex and the transition state are stabilized by three H-bonds, forming a seven member ring-like structure. We also investigated the reaction of OH radicals with the two $C_4H_8O_2$ isomers; methyl propionate ($CH_3CH_2C(O)OCH_3$) and ethyl acetate ($CH_3C(O)OCH_2CH_3$) (3). In ethyl acetate the H-abstraction was computed to occur exclusively (~99%) at the $–OCH_2$- group (3). In contrast, both methyl groups and the $–CH_2–$ group contribute appreciably in the reaction of OH with methyl propionate. In general H-abstraction from the $–C(O)OC\mathbf{H_2}$- dominates and only in the case of methyl esters (R = CH_3) does H-abstraction from the beta carbon position of $–C\mathbf{H_2}CH_2(O)OR$- dominate .

References

(1) Andersen, V.F.; Nilsson, E.J.K.; Jørgensen, S.; Nielsen, O.J.; Johnson, M.S. *Chem. Phys. Lett.* **2009,** 472, 23-29.
(2) Jørgensen, S.; Andersen, V.F.; Nilsson, E.J.K.; Nielsen, O.J.; Johnson, M. S. *Chem. Phys. Lett.*, **2010,** 490, 116-222.
(3) Andersen, V.F.; Berhanu, T.A.; Nilsson, E.J.K.; Jørgensen, S.; Nielsen, O.J.; Wallington, T.J.; Johnson, M.S. *J. Phys. Chem. A,* **2011**, 115, 8906-8919.
(4) Andersen, V.F.; Ørnsø, K.B.; Jørgensen, S.; Nielsen, O.J.; Johnson, M. S. *Submitted to J. Phys. Chem. A* **2012**.

Low temperature oxidation of butanol: theoretical kinetic modeling

Tatsuo Oguchi,[1*] Motoki Ito,[1] and Akira Miyoshi[2]

[1] Toyohashi University of Technology, Toyohashi, Aichi, JAPAN
[2] The University of Tokyo, Bunkyo-ku, Tokyo, JAPAN
* Corresponding author: oguchi@tut.jp

Low temperature oxidation mechanism of 2-butanol was investigated theoretically. The reaction paths for oxidation of some hydroxybutyl radicals formed from 2-butanol were followed by CBS-QB3 level energy calculations as:

$$\begin{array}{llr}
CH_3C(OH)CH_2CH_3 + O_2 & \rightarrow CH_3C(OH)(OO)CH_2CH_3 & (1) \\
CH_3C(OH)(OO)CH_2CH_3 & \rightarrow CH_3C(O)CH_2CH_3 + HO_2 & (2)
\end{array}$$

and

$$\begin{array}{llr}
CH_3CH(OH)CHCH_3 + O_2 & \rightarrow CH_3CH(OH)CH(OO)CH_3 & (3) \\
CH_3CH(OH)CH(OO)CH_3 & \rightarrow CH_3CH(O)CH(OOH)CH_3 & \\
 & \qquad \rightarrow CH_3CHOOH + CH_3CHO & (4a) \\
 & \rightarrow CH_2CH(OH)CH(OOH)CH_3 & \\
 & \qquad \rightarrow CH_3CHOOH + CH_2CHOH & (4b) \\
 & \rightarrow CH_3C(OH)CH(OOH)CH_3 & \\
 & \qquad \rightarrow CH_3C(OH)CH(\text{-}O\text{-})CH_3 + OH & (4c).
\end{array}$$

Other reaction paths were also examined, however, considerable reaction path was not found. Canonical variational TST calculation on the calculated minimum energy path for reaction 1, 3 and multi-well, multi-channel RRKM calculation were performed for the reactions 1-4 to obtain the reaction rate constants. The first formally direct reaction mechanism (the reaction 1 and successive reaction 2) were highly exothermic (~110 kJ mol^{-1}) and barrierless reaction, so that the rate constant was very large ($1\text{-}10 \times 10^{-11}$ cm^3 s^{-1}) even at room temperature and little dependency for pressure and temperature was found. On the other hand, the branching fractions of the reaction 4a-4c and competitive stabilization channel strongly depend on the total pressure and temperature. However, reaction 4a was most important path at any pressure under the 900 K temperature range because indirect reaction 4a was also dominant (ϕ~0.7) for overall unimolecular reaction of the stabilized peroxy radical. The rate constants obtained in this study were applied for detailed kinetic modeling for auto-ignition of butanols.

This work was partly supported by Grants-in-Aid for Scientific Research (B) #23360091, JSPS, Japan.

Shock Tube Studies on the Decomposition of 2-Butanol

Claudette M. Rosado-Reyes*, and Wing Tsang

National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA
* Corresponding author: claudette.rosado-reyes@nist.gov

This work is aimed at providing fundamental or transferable chemical kinetics data for biofuels to combustion databases, for prediction purposes. The amount of kinetic information needed for simulation is immense, making not possible to have experimental measurements for every reaction. A striking example is the case of mixtures. Any possible use of biofuels will be in combination with petroleum based substances. Fundamental information represents data that lead directly to mixing rules that cannot be determined on any other basis. The greatest difference in the fundamental reaction processes between any two fuels is the initial radical formation and decomposition processes. Once the primary radicals are formed upon initial thermal decomposition, their subsequent reactions become increasingly similar as combustion progresses ultimately leading to the production of carbon dioxide, water or soot. Much of the existing kinetic databases are based on rate rules derived either empirically or through ab-initio calculations. The uncertainties in these estimates are vague. This is especially the case as fuel molecules become larger. Unambiguous experimental results are important not only for the purposes of simulations but also as a basis for calibrating estimates.

The experiments were carried out in a heated single pulse shock tube(1). The key features of these experiments are the dilute concentrations of the test mixture, of the order of 500 ppm 2-butanol, and the large excesses of a chemical inhibitor, 1% 1,3,5-trimethylbenzene. The chemical inhibitor captures all the reactive radicals that are formed, thus only unimolecular reactions contribute to the product yields. This internal standard approach makes certain that the non-idealities in the shock tube study are experienced by both target molecules. Therefore results from the shock tube study are traceable and transferable and provide the basic information necessary for developing the relationships between the behaviors of all fuels that have been studied.

The determined rate expressions for main initial decomposition processes in 2-butanol are,

$$k\,(C_3H_6(OH)CH_3 \rightarrow \text{(Z)-}CH_3CH{=}CHCH_3 + H_2O) = 1.41\times10^{13}\exp(-33414/T[K])\ s^{-1}$$
$$k\,(C_3H_6(OH)CH_3 \rightarrow \text{(E)-}CH_3CH{=}CHCH_3 + H_2O) = 2.90\times10^{13}\exp(-33820/T[K])\ s^{-1}$$
$$k\,(C_3H_6(OH)CH_3 \rightarrow CH_3CH_2CH{=}CH_2 + H_2O) = 3.57\times10^{13}\exp(-33002/T[K])\ s^{-1}$$
$$k\,(C_3H_6(OH)CH_3 \rightarrow CH_3CH_2{*} + {*}CH(OH)CH_3 = 7.40\times10^{15}\exp(-39252/T[K])\ s^{-1}$$

Comparison with estimates in the literature illustrates the diversity of the predictions based on various methodologies, with no any obvious internal consistencies.

The present results are compared with earlier data from single pulse shock tube studies on other larger alcohols(2,3). Water elimination is a major channel. General trends with respect to methyl substitution can be derived. The dependence on methyl ejection is however much weaker than the in alkyl halides. An OH group adjacent to the bond being broken increases the rate constants for bond breaking. The presence of the OH group beta to the bond being broken has negligible effects.

References

(1) Awan, I.A.; McGivern, W.S.; Tsang, W.; Manion, J.A. *J. Phys. Chem. A* **2010**, 144, 7832-7846.

(2) Rosado-Reyes, C.M.; Tsang W.”Shock Tube Study on the Thermal Decomposition of n-Butanol”, *Proceedings of the Combustion Institute,* submitted.

(3) Tsang, W. *Int. J. Chem. Kinet.* **1976**, 8, 173-192.

Rate coefficient measurements of the OH + *n*-, *i*-, *s*-, and *t*-butanol gas-phase reactions between 220–380 K: non-Arrhenius behavior and competitive reaction mechanisms

Max R. McGillen,[1,2] Munkhbayar Baasandorj,[1,2] and James B. Burkholder[2,*]

[1] Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO, USA
[2] National Oceanic and Atmospheric Administration (NOAA), Boulder, CO, USA
* Corresponding author: james.b.burkholder@noaa.gov

Butanols are poised to become a major alternative to fossil fuel gasoline formulations with widespread usage. As a result, the emission of butanol into the atmosphere is likely to increase with time and it may impact the oxidative capacity of the troposphere and ozone production. The reaction of butanol with the OH radical is expected to be its dominant loss process in the atmosphere. In this work, reaction rate coefficients for the *n*-, *i*-, *s*-, and *t*-butanol isomers with the OH radical were measured under *pseudo*-first-order conditions in OH using pulsed laser photolysis to produce OH radicals and laser induced fluorescence to monitor its temporal profile. Rate coefficients were measured over the temperature range 220 to 381 K at total pressures between 50 and 200 Torr (He). Each of the butanol isomers exhibited a non-Arrhenius temperature dependence and no dependence on pressure.

The observed non-Arrhenius temperature dependence was interpreted as the result of a competition between reactive sites possessing different activation energies and pre-exponential factors. The results from this work were combined with available literature data from high temperature shock tube studies (~1200–1800 K) and room temperature reaction product yield studies and guided by structure-activity relationships to derive a self-consistent set of site specific temperature dependent reactivities between 220 to 1800 K. The strengths and weaknesses of this semi-empirical approach as well as possible explanations for the observed enhanced reactivity at temperatures relevant to the chemistry of the upper troposphere lower stratosphere will be discussed.

Experimental Investigation of Ignition of Second-Generation Biofuels at High Pressures

C. Lee[*], S. Vranckx, H. K. Chakravarty, and R. X. Fernandes

Physico-Chemical Fundamentals of Combustion, RWTH Aachen University, Aachen, Germany
* Corresponding author: lee@swl.rwth-aachen.de

In recent years, the interests in biomass derived fuels as alternatives or additives to conventional fuels have been increasing to reduce the dependence on fossil fuels supplies and address the increasing concern of global warming. Especially the interest of using second-generation biofuels, as oxygenates in gasoline has increased over the years due to their significant advantages over first-generation biofuels. As an example, 2,5-dimethylfuran(DMF) has an energy density 40% higher than ethanol [1]. More attractively, 2,5-DMF consumes only one-third of the energy in the evaporation stage of its production. Additionally recent remarkable breakthroughs in the mass production technology of 2,5-DMF have been reported [2]. Our interests are to assess the combustion characteristics of furan based biofuels for their optimal performance in advanced combustion technologies by developing detailed, highly validated and predictive chemical kinetic models.

This work presents the experimental determination of auto-ignition delay times of several saturated & unsaturated furan derivates (Furan, 2-Methylfuran, 2,5-DMF, Tetrahydrofuran) at intermediate and low temperatures and high pressures. Experiments are performed in a Rapid Compression Machine (RCM) and ignition delay times are determined using pressure histories in the temperature range from 650 – 920 K and pressures from 10 – 40 bar. Variable fuel-oxygen concentrations are used in order to determine the influence of equivalence ratios on the ignition delays.

Detailed chemical kinetic models are developed and optimized by refining rate parameters of sensitive reactions based on first principles. A comparison of the performance of the optimized kinetic models with diverse experimental data is presented.

This work has been performed within the Cluster of Excellence “Tailor Made Fuels from Biomass”, which is funded by the Excellence Initiative by the German federal and state governments to promote science and research at German Universities. Support from the Alexander von Humbolt (AvH) foundation through a Postdoctoral Fellowship for S. Vranckx is gratefully acknowledged.

References

(1) Binder, J.B.; Raines, R.T. *J. Am. Chem. Soc*. **2009**, 131, 1979-1985.
(2) Roman-Leshkov, Y.; Barrett, C.J.; Liu, Z.Y.; Dumesic, J.A. *nature*. **2007**, 447, 982-985.

Global Sensitivity Analysis of the Butanol Combustion Mechanism

Dingyu D. Y. Zhou,[1] Rex T. Skodje,*[2] and Michael J. Davis

[1] Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, USA
[2] Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne IL, USA
* Corresponding author: Rex. skodje@colorado.edu

Butanol has become the focus of recent interest as a potential biofuel. As such, it is important to develop reliable butanol combustion models to aid in the optimization of the combustion conditions and the design of fuel blends. We have recently developed a new technique to systematically improve chemical kinetic models using first global sensitivity analysis to identify key reaction steps, followed by high level theoretical modeling to improve the rate coefficients for targeted reactions.(1,2) In the present work we apply this mechanism improvement scheme to the 1600 reversible-step butanol combustion model of Curran and coworkers (3). It is found that the HO_2+n-C_4H_9OH reaction is most crucial in setting the ignition delay time. However, other steps are identified as more important for the growth of measurable intermediate species in the pre-ignition phase of the kinetics. It is shown that model is improved by the theoretical update of the targeted reactions.

References

(1) R. T. Skodje, A. S. Tomlin, S. J. Klippenstein, L. B Harding, and M. J. Davis, "Theoretical Validation of Chemical Kinetic Mechanisms: Combustion of Methanol", J. Phys. Chem. A. 114, 8286 (2010).

(2) D. D. Y. Zhou, M. J. Davis. and R. T. Skodje, "Global Sensitivity Analysis and Model Improvement of a Butanol Combustion Model", to be submitted.

(3) G. Black, H. J. Curran, S. Pichon, J. M. Simmie, and V. Zhukov, "Bio-butanol: Combustion Properties and Detailed Chemical Kinetic Model", Combustion and Flame 157, 363 (2010).

Kinetic studies of the oxidation of a series of aldehydes in a jet-stirred reactor. Experiments and modeling.

Philippe Dagaut,[1,*] Guillaume Dayma,[1,2] and Casimir Togbé[1]

[1] CNRS-INSIS, Orléans, France
[2] University of Orléans, Faculté des Sciences, France
* Corresponding author: dagaut@cnrs-orleans.fr

There is a strong drive towards utilizing oxygenated biofuels, such as alcohols, in blends with conventional fossil fuels. Improving the kinetic modeling of the oxidation of these bio-derived alcohols requires further investigation of their key stable intermediates such as the aldehydes. In this study, an experimental and chemical kinetic modeling investigation of several aldehydes oxidation was carried out. Experiments were conducted in a jet stirred reactor over a wide range of equivalence ratios (0.5-2), temperatures (530-1200 K), and pressure (1-10 atm). Stable species concentration profiles were measured in the jet stirred reactor. A detailed chemical kinetic reaction model was validated using the present experimental results and existing literature data. The model was used also to provide insight into the controlling reaction pathways for aldehydes oxidation.

MECHANISM OF THE THERMAL DECOMPOSTION OF BENZALDEHYDE

AnGayle Vasiliou[1,2], Mark R. Nimlos[2], John W. Daily[1] and
G. Barney Ellison[1]

[1] University of Colorado, Boulder, CO, USA
[2] National Renewable Energy Laboratory, Golden CO, USA

We have used a microtubular reactor to study the pyrolysis of benzaldehyde, and furfural. Samples of 1% organic substrate in 1 or 2 atm of a rare gas (He or Ar) are heated in a tubular reactor. The reactor is a 1 mm diam x 3 cm long silicon carbide tube. The walls of the SiC tube are resistively heated to temperatures up to 1700 K for the last 2 cm of the reactor. The residence times of substrates in the heated reactor are about 50 -100 μsec. Gases emerging from the SiC reactor enter a vacuum chamber with a background pressure of 1 x 10(- 5) Torr. As the molecules emerge from the SiC tube into the vacuum, the supersonic expansion cools the beam to rotational temperatures of roughly 100 K. We have used computational fluid dynamics to characterize the properties of the gas flow through the hot SiC tubular reactor. Molecular fragments resulting from thermal cracking of the substrates are identified by two independent methods: VUV photoionization mass spectroscopy and infrared absorption. The skimmed molecular beam is intersected by the 9th harmonic of a YAG laser at 118.2 nm (10.487 eV) and ionized. The resultant ions are detected by time-of-flight mass spectroscopy. In addition to PIMS detection, we also capture the molecular beam on a CsI window cooled to 20 K. Molecules trapped in these cryogenic rare-gas matrices are analyzed by infrared absorption spectroscopy. Benzaldehyde and furfural are pyrolysis products that result from sugars. We have observed that heating these heterocyclic aromatic compounds decomposes them to C_6H_6 CH_3CCH, CO, CH_2CCO, and HCCH. propargyl radicals, $HCCCH_2$. Benzaldehyde decarbonlaytes to produce benzene and furfural decarbonlaytes to produce furan.

Reactions of the CH Radical with Hydrocarbons Involved in Biofuel Combustion

Jessica F Lockyear,[1*] Fabien Goulay,[2] and Stephen R Leone[1,3]

[1] Lawrence Berkeley National Laboratory, Berkeley, CA, USA
[2] Department of Chemistry, West Virginia University, Morgantown, WV, USA
[3] Department of Chemistry, University of California at Berkeley, Berkeley, CA, USA
* Corresponding author: JFLockyear@lbl.gov

Combustion involves many short-lived, excited state species and highly reactive radicals; one such species is the methylidyne radical (CH). The CH radical is extremely reactive due to the presence of one singly occupied and one vacant non-bonding orbital on the carbon. This radical has been detected in combustion environments in myriad studies[1,2] and plays a critical role in kinetics of NO_x formation and destruction.[1] The primary formation mechanism for CH in non-premixed fuel flames is the reaction between CH_2 and OH yielding CH and H_2O.[1] With regards to reactivity, the CH radical is known to undergo very rapid insertion-elimination reactions with unsaturated hydrocarbons, often close to the diffusion-limited rate.[3] Insertion of the CH radical into either π or σ molecular sites followed by H- or H_2-elimination contributes to molecular growth. Alternatively, CH_3-elimination proffers a route to functional group change.

There is currently a growing shift away from petroleum-based fuels towards biofuels derived from biomass and micro-algal oils.[4] World biodiesel production for transport fuel expanded eleven-fold between 2000 and 2007 from 1 billion to almost 11 billion litres.[5] Biodiesel comprises highly oxygenated unsaturated species, predominantly esters. It is the presence of these oxygenated functional groups that dramatically reduces particulate and soot emissions.[6] Currently, our understanding of how functional groups are interchanged by reaction with CH is almost non-existent. Studies of several reactions of this type have been carried out employing the synchrotron radiation from the Advanced Light Source in conjunction with a multiplexed photoionization mass spectrometer. Specifically, CH + acrolein, CH + oxirane and CH + dimethylether have been investigated. Where unsaturated bonds are present the chemistry is very complex and in the case of acrolein, the CH readily inserts into either the C=O or C=C bonds, resulting in a wide variety of reaction products. The mechanisms of such reactions have been elucidated *via* selective deuteration of the reactants, thus a deep understanding of the dynamics has been achieved. These insights may help to predict the chemistry that will occur during combustion between molecules that cannot be experimentally investigated. Moreover, employing the tunable synchrotron radiation has yielded quantitative branching ratios, obtained for the first time for these reactions and which are invaluable for combustion modeling.

References

(1) Naik, S.V. and Laurendeau, N.M. *Appl. Phys. B-Lasers Opt.* **2004**, 79, 891-905.
(2) Kohler, M.; Brockhinke, A.; Braun-Unkhoff, M. and Kohse-Hoinghaus, K. *J. Phys. Chem. A* **2010**, 114, 4719-4734.
(3) Goulay, F.; Trevitt, A.J.; Meloni, G.; Selby, T.M.; Osborn, D.L.; Taatjes, C.A.; Vereecken, L. and Leone, S.R. *J. Am. Chem. Soc.* **2009**, 131, 993-1005.
(4) Zador, J.; Taatjes, C.A. and Fernandes, R.X. *Prog. Energy Combust. Sci.* **2011**, 37, 371-421.
(5) Towards sustainable production and use of resources: Assessing Biofuels, Bringezu, S.; Shutz, H.; O'Brien, M.; Kauppi, L.; Howarth, R. and McNeely, J., *United Nations Environment Programme*, 978-92-807-3052-4.
(6) Graboski, M.S. and McCormick, R.L. *Prog. Energy Combust. Sci.* **1998**, 24, 125-164.

Theoretical study of thermal decomposition of biodiesel fuels

Mohamad Akbar Ali and Angela Violi*

Department of Mechanical Engineering, University of Michigan, Ann Arbor, MI 48109, USA

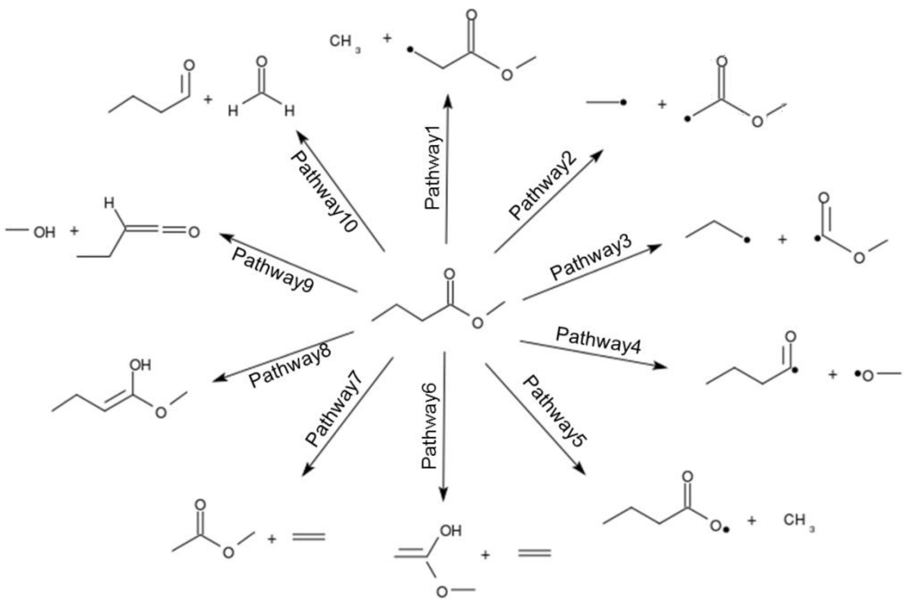
The use of petroleum-based fuels in the transport sector has raised issues such as air pollution, energy security, and substantial emission of CO_2, which is linked to climate change. Due to the extensive use of these fuels, researchers are motivated to look for alternative solutions. One of the potential alternative fuels that has been suggested is biofuels. Biofuels are comprised of a mixture of saturated and unsaturated alkyl esters, containing long carbon chains with 16-18 carbon atoms, which are typically derived from vegetable oils and animal fats. These fuels introduce new challenges for the development of chemical reaction mechanisms. Namely, due to the complexity of biofuels molecules, a very large number of reactions are usually required to create kinetic mechanisms for these fuels directly. As a result, simpler molecules are typically chosen to represent the chemical properties of real fuels. Methyl butanoate (MB), is an example of a simple methyl ester that has been suggested to be a convenient alternative for large biofuel molecules. Ab initio methods, namely, high level quantum composite G3B3 and CASSCF methods calculated accurate energies; Variational Transition State Theory, Rice-Ramsperger-Kassel-Marcus (RRKM) and master equation (ME) simulations provided temperature and pressure dependent reaction rate constants.

References

[1] Fisher, E.M.; Pitz, W.J.; Curran, H.J.; Westbrook, C.K. *Proc. Combust. Inst.* **2000**, 28, 1579-1586.

[2] Lai, J.Y.W.; Lin, K.C.; Violi, A. *Progress in Energy and Combustion Science*, **2011**, 37, 1-14

Thermal decomposition of methyl butanoate



Accuracy of OH Reaction Rate Constants Determination over Atmospheric Temperatures.

Vladimir L. Orkin,[1,*] Victor G. Khamaganov,[1] Larissa E. Martynova,[1]
and Michael J. Kurylo[2]

[1] National Institute of Standards and Technology, Gaithersburg, MD, USA
[2] Goddard Earth Sciences and Technology (GEST) Center, Greenbelt, MD, USA
* Corresponding author: vladimir.orkin@nist.gov

One of the most important parameters in estimating the environmental impact due to emission of a compound is its residence time in the atmosphere, which is driven by the reaction of a compound with hydroxyl radicals (OH) for many atmospheric trace gases. The atmospheric lifetime is important for estimating ozone depletion potential (ODP) and global warming potential (GWP) of industrial compounds which are needed for evaluation of their environmental impact and regulatory purposes.

The sources of critically evaluated photochemical data for atmospheric modeling, NASA/JPL Publications and IUPAC Publications, recommend uncertainties within 10%-60% for the majority of OH reaction rate constants with only a few cases where uncertainties lie at the low end of this range. These uncertainties can be somewhat conservative because evaluations are based on the data from various laboratories obtained during the last few decades. Nevertheless, even the authors of the original experimental works rarely estimate the total combined uncertainties of the published OH reaction rate constants to be less than ca. 10%. Thus, uncertainties in the photochemical properties of potential and current atmospheric trace gases obtained under controlled laboratory conditions still may constitute a major source of uncertainty in estimating the compound's environmental impact.

The purpose of the presentation is to illustrate the potential for obtaining more accurate laboratory OH reaction rate constant data over the temperature range of atmospheric interest. Both data scattering and systematic uncertainty associated with instrumental measurements contribute to the total uncertainty of the rate constant. Although data scattering does not obviously obey the normal distribution, the statistical uncertainty is usually calculated to present the results of kinetic measurements. The scattering of measured rate constants in the Arrhenius plot should be consistent with their individual uncertainties and can serve as complementary evidence of the measurement precision. Then, the statistical tests can be applied to proof the temperature dependence derived from the fit to the experimentally obtained data. The detailed inventory of various sources of instrumental uncertainty yields the total uncertainty of the OH reaction rate constant, which can be as small as ~2% in our flash photolysis – resonance fluorescence experiments.

The high precision of kinetic measurements allows reliable determination of weak temperature dependences of the rate constants and clear resolution of the curvature of the Arrhenius plots for the OH reaction rate constants of various compounds. The results of OH reaction rate constant determinations between 220 K and 370 K will be presented.

References

(1) Orkin, V.L.; Martynova, L.E.; Ilichev, A.N. *J. Phys. Chem. A* **2010**, 114, 5967-5979.
(2) Orkin, V.L.; Khamaganov, V.G.; Martynova, L.E.; Kurylo, M.J. *J. Phys. Chem. A* **2011**, 115, 8656-8668.

Reversible reactions of OH with methylated benzenes and contributions of ipso addition

Paulo Alarcón,[1] Jannis von Buttlar,[1] Birger Bohn,[2,3] Rainald Koch,[1,3] Manfred Siese,[1,3] Ralf Knispel,[3] Franz Witte,[3] Cornelius Zetzsch[1,3,*]

[1] Laboratory for Atmospheric Chemistry Research, BayCEER, University of Bayreuth, Germany
[2] Forschungszentrum Jülich GmbH, IEK-8: Troposphäre, Jülich, Germany
[3] formerly: Fraunhofer Institute for Toxicology and Aerosol Research, Hannover, Germany
* Corresponding author: Cornelius.Zetzsch@uni-bayreuth.de

The reversible addition of OH radicals to the methylated benzenes toluene, p-xylene, all three trimethylbenzenes, 1,2,4,5-tetramethylbenzene, pentamethylenzene, and hexamethylbenzene has been studied by VUV flash photolysis of H_2O in the presence of the aromatic at various temperatures in inert buffer gas, monitoring OH by time resolved resonance fluorescence. A reversible reaction of OH with hexamethylbenzene, observed by the same technique by Koch et al. [1] and von Buttlar et al. [2], implies that ipso addition to a fully substituted aromatic can be a rapid process in the gas phase.

In general, addition in competition with abstraction leads to biexponential decays of OH as soon as it becomes reversible on the time scale of the observation. The decays may become triexponential if only two types of reversible addition (ortho and ipso) exist by symmetry. This has been shown for trimethylbenzene (1,3,5-) by Bohn and Zetzsch [3], where the other isomers (1,2,3- and 1,2,4-) follow a similar behavior with two predominating adducts. Meanwhile we observed such behavior of OH with 1,2,4,5-tetramethylbenzene (only ortho and ipso available, see *Alarcon et al., this conference*) and a similar behavior with pentamethylbenzene according to the mechanism

$$\text{OH + aromatic} \leftrightarrows \text{ortho-adduct } (k_a\,,\, k_{-a}) \qquad \text{(a)}$$
$$\text{OH + aromatic} \leftrightarrows \text{ipso-adduct } (k_b\,,\, k_{-b}) \qquad \text{(b)}$$
$$\text{OH + aromatic} \rightarrow \text{products } (k_c) \qquad \text{(c)}$$

where isomerizations of the adducts cannot be excluded. We present determinations of Arrhenius parameters for the reversible additions.

References

(1) Koch, R.; Knispel, R.; Elend, M.; Siese, M.; Zetzsch, C. *Atmos. Chem. Phys.* **2007**, 7, 2057-2071.
(2) von Buttlar, J.; Koch, R.; Siese, M.; Zetzsch, C. *Geophys. Abstr.* **2008**, 10, EGU2008 – 10576.
(3) Bohn, B.; Zetzsch, C. *J. Phys. Chem. A* **2012** (submitted for publication).

Compared reactivity of the OH-initiated tropospheric degradation of a series of methylated benzenes from benzene to hexamethyl-benzene. A theoretical approach

Marie-Thérèse Rayez[1,*], Jean Claude Rayez[1] and E. Villenave[2]

1 University of Bordeaux, ISM (CNRS UMR 5255), 33405 Talence cedex, FRANCE

2 University of Bordeaux, EPOC-LPTC (CNRS UMR 5805), 33405 Talence cedex – FRANCE

* Corresponding author mt.rayez@ism.u-bordeaux1.fr

This study aims at a better understanding of the OH-initiated tropospheric degradation of aromatic hydrocarbons. Although this field of research has attracted a lot of attention in the last decades, there are still many open questions regarding important details of the reaction mechanism. In particular, in the case of substituted aromatics, there is increasing evidence in recent literature for the formation of ipso-type radical adducts (addition at ring position already occupied by a substituent): this possible reaction pathway has not been considered before in atmospheric chemistry models.

In this work, we used quantum chemistry methodology (DFT-M06-2X/6-31G(d,p)) coupled to kinetic calculations to put some light on the reaction of a series of methylated benzenes from benzene to hexamethyl-benzene with OH radicals. We have considered all the possible addition pathways. One of the most important results that we have obtained is that ipso addition can be anticipated to be the predominant pathway in OH-addition reactions of some of the methylated benzenes.

A detailed analysis of the electronic properties has allowed us to interpret the results and build Structure Activity Relationships (SAR). A comparison with the few available experimental studies has been done.

Rate constants for the reaction of OH with durene (1,2,4,5-tetramethylbenzene), leading to two types of adducts: ortho and ipso.

Paulo Alarcón,[1] Birger Bohn[2], Cornelius Zetzsch[1,3]

[1] Laboratory for Atmospheric Chemistry Research, University of Bayreuth, Germany
[2] Forschungszentrum Jülich GmbH, IEK-8: Troposphäre, Jülich, Germany
[3] Fraunhofer Institute for Toxicology and Experimental Medicine, Hannover, Germany
* Corresponding author: cornelius.zetzsch@uni-bayreuth.de

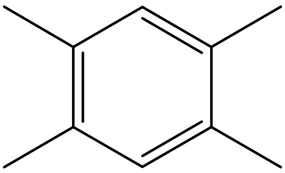
The high symmetry of durene (1,2,4,5-tetramethylbenzene) leads to identical electronic configurations at the four positions of the aromatic ring occupied by methyl groups - different from the two unoccupied positions, which are identical as well. The addition of OH radicals to these two types of positions (ortho and ipso) was studied by VUV flash photolysis of H_2O in the presence of durene between 300 and 353 K in He, monitoring OH by time resolved resonance fluorescence.

Reversible addition in competition with abstraction leads to biexponential decays of OH in general and has hitherto been observed for almost every aromatic in the temperature range where addition becomes reversible on the time scale of the observation. A rapid, reversible addition of OH to the six ipso positions of hexamethylbenzene is already known (Koch et al., 2006). Two types of reversible addition (ortho and ipso) have been recently distinguished for mesitylene (1,3,5-trimethylbenzene) by quantitative evaluation of triexponential decays of OH (Bohn and Zetzsch, 2012). The other isomeric trimethylbenzenes (1,2,3 and 1,2,4) follow a similar behavior with two predominating adducts (Bohn and Zetzsch, 2012). Measurements for OH + durene follow the same mechanism

$$\text{OH + durene} \leftrightarrows \text{ortho-adduct } (k_a\,,\, k_{-a}) \qquad (1)$$

$$\text{OH + durene} \leftrightarrows \text{ipso-adduct } (k_b\,,\, k_{-b}) \qquad (2)$$

$$\text{OH + durene} \rightarrow \text{products } (k_c) \qquad (3)$$



Durene: 1,2,4,5 - tetramethylbenzene

and are evaluated for the total of the abstraction and both addition paths ($k_a+k_b+k_c$), decreasing from 5.3 x 10^{-11} cm^3 s^{-1} at room temperature to 2.5 x 10^{-11} cm^3 s^{-1} at 353 K. Activation energies for the product of the forward and backward reaction of each adduct were measured. Using some approximations, activation energies for each reaction can be estimated, as well as the equilibrium constant for the more energetic adduct.

R. Koch, R. Knispel, M. Elend, M. Siese, C. Zetzsch (2007) **Atmos. Chem. Phys.,** 7, 2057-2071

B.Bohn, C.Zetzsch (2012). Submitted for publication.

Atmospheric Chemistry of Allyl Halides: Temperature and Pressure Dependent Rate Coefficients for the Gas Phase Reactions of OH Radicals and Cl Atoms with X-$CH_2CH=CH_2$ (X: Cl, Br, I)

Vassileios G. Stefanopoulos,[1] Vassileios C. Papadimitriou,[1] and Panos Papagiannakopoulos[1,*]

[1] University of Crete, Department of Chemistry, Heraklion, Greece
* Corresponding author: panosp@chemistry.uoc.gr

Two complementary experimental techniques were employed, in this work, to study the kinetics and the mechanism for the gas phase reactions of the major atmospheric oxidants, OH radicals and Cl atoms, with an allyl halides series, X-$CH_2CH=CH_2$ (X:Cl, Br and I), as a function of temperature (258 -365 K) and pressure (2×10^{-3} – 700 Torr). In particular, the zero pressure limit (~2 mTorr) rate coefficients for the Cl reactions were measured using the continuous-flow absolute rate method of Very Low Pressure Reactor (Knudsen Cell), coupled with quadrupole mass spectrometry (VLPR/QMS),[1] at T = 298 K. The OH and Cl pressure dependent rate coefficients (25 – 700 Torr) were measured employing the static relative rate method of the Thermostated PhotoChemical Reactor equipped with Fourier Transformed InfraRed Spectroscopy (TPCR/FTIR),[2] in the temperature range 260 – 365 K. Products were monitored with both FTIR spectroscopy and Mass spectrometry, and it was revealed that the association mechanism dominates over the potent abstraction reaction pathways, in consistence with the observed pressure (Cl reactions) and inverse to temperature dependence (both Cl and OH reactions) rate coefficient measured in the present study. Finally, IR cross sections were also determined and the Global Warming Potentials (GWP) of the studied allyl halides were estimated employing Pinnock model,[3] in a 20 years time-horizon, using rate coefficients and cross section measured in this work.

References

(1) Papadimitriou,V.C.; Papanastasiou, D.K.; Stefanopoulos, V.G.; Zaras, A.M.; Lazarou, Y.G.; Papagiannakopoulos, P. *J. Phys. Chem. A* **2007**, 111, 11608 – 11617.
(2) Romanias, M.N.; Stefanopoulos, V.G.; Papanastasiou, D.K.; Papadimitriou,V.C.; Papagiannakopoulos, P. *Int. J. Chem. Kin.* **2010**, 42, 724 – 734.
(3) Pinnock, S.; Hurley, M.D.; Shine, K.P.; Wallington,T.J.; Smyth, T.J. *J. Geophys. Res.* **1995**, 100, 23227 – 23238.

Kinetic study on the reaction of $CF_3CH=CH_2$ with Cl atoms in a smog chamber

María Rosario Martín-Luengo,[1] Bernabé Ballesteros,[1,2*] Thomas M. Townsend,[2] Elena Jiménez,[2] and José Albaladejo[2*]

[1] Instituto de Combustión y Contaminación Atmosférica. Universidad de Castilla – La Mancha. Camino Moledores s/n, 13071 Ciudad Real. Spain.
[2] Departamento de Química Física. Facultad de Ciencias y Tecnologías Químicas. Universidad de Castilla – La Mancha. Avenida Camilo José Cela, s/n. 13071 Ciudad Real. Spain.
* Corresponding authors: Jose.Albaladejo@uclm.es, Bernabe.Ballesteros@uclm.es

Recognition of the adverse environmental impact of chlorofluorocarbons (CFCs) released into the atmosphere [1,2] has led to an international effort to replace these compounds with environmentally acceptable alternatives. Saturated hydrofluorocarbons (HFCs) have become widely used CFC replacements. Unsaturated hydrofluorocarbons are a class of compounds, which are potential replacements for CFCs and saturated HFCs in air conditioning units.
In this work, the rate coefficient, k_{Cl}, for the reaction of $CF_3CH=CH_2$ with Cl atoms at room temperature and 720 Torr of air is measured using a relative kinetic technique:

$$Cl + CF_3CH=CH_2 \rightarrow \text{Products} \qquad k_{Cl} \qquad (1)$$

Chlorine atoms are generated by UV photolysis of Cl_2 and the loss of $CF_3CH=CH_2$ and the reference compound (propene or 1,3-butadiene) and are monitored by both FTIR and GC-FID.
Two kinetic studies of reaction (1) were found in the literature. Sulbaek Andersen et al. [3] reported a relative rate coefficient of $(9.07 \pm 1.08) \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1} in 700 Torr of N_2 or N_2/O_2 at 296 ± 1 K. These authors also used FTIR spectroscopy as a detection technique. Takahashi et al. [4] employed the pulsed laser photolysis/ vacuum ultraviolet laser-induced fluorescence techniques to study the kinetics of reaction (1) at low pressure (9.1 Torr of CF_4) at 295±2 K. The absolute k_{Cl} reported by Takahashi et al., $(4.49\pm0.64) \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1}, was found to be half of that reported by Sulbaek Andersen et al. [3].
Additionally, in this work the products of the reaction are investigated by GC-MS and SPME. The atmospheric implications of the Cl reactivity are also discussed in terms of its lifetime and detected products.

References

(1) Molina, M.J., Rowland, F.S., *Nature* **1974**, 249, 810-812.
(2) Farman, J.D., Gardiner, B.G., Shanklin, J.D., *Nature* **1985**, 315, 207-210.
(3) Sulbaek Andersen, M.P., Nielsen, O.J., Toft, A., Nakayama, T., Matsumi, Y., Waterland, R.L., Buck, R.C., Hurley, M.D., Wallington, T.J., *J. Photochem. Photobiol. A: Chem.* **2005**, 176, 124-128.
(4) Takahashi, K., Iwasaki, E., Nakayama, T., Matsumi, Y., Wallington, T.J., *Int. J. Chem. Kinet.* **2007**, 39, 328-332.

Atmospheric Chemistry of Halogenated Propenes

Mads P. Sulbaek Andersen[1,*], Timothy J. Wallington[2], Ole J. Nielsen[3], S. P Sander[1]

[1] Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Mail Stop 183-901, Pasadena, CA 91109, USA
[2] System Analytics and Environmental Sciences Department, Ford Motor Company, Mail Drop RIC-2122, Dearborn, MI 48121-2053, USA
[3] Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

* Corresponding author: mads@sulbaek.dk

FTIR-smog chamber techniques were used to study the kinetics, products and mechanisms of the Cl atom and OH radical initiated oxidation of a number of halogenated propenes in 700 Torr of air or N_2/O_2 diluent at 296 ± 2 K. The reactions of Cl atoms and OH radicals with halogenated propenes occur via addition to the C=C double bond. Reaction with OH radicals is the major atmospheric sink for halogenated propenes. Infrared spectra, radiative efficiencies, and global warming potentials of the halogenated propenes are reported. The contribution of halogenated propenes to radiative forcing of climate change and to local air pollution is negligible. The results are discussed with respect to the atmospheric chemistry and environmental impact of halogenated alkenes.

Pressure and Temperature Dependent Study of the $CH_3C(O)O_2$ + HO_2 Reaction Branching Ratio Using the Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC)

F. Winiberg[1*], S. C. Smith[2], T. Dillon[3], C. Gross[3] and P. W. Seakins[1]
[1] University of Leeds, Leeds, UK
[2] CIRES, Boulder, Colorado, USA
[3] MPI, Mainz, Germany
*Corresponding author: chm5fafw@leeds.ac.uk

Organic peroxy radicals, RO_2, play a key role in the tropospheric HO_x (OH and HO_2) cycle. Oxidation of Volatile Organic Compounds (VOCs) lead to the creation of RO_2 and HO_2 radicals. These products are known to react together, with three possible pathways: (A), (B) and (C). The branching ratio for these reactions is dependent on the structure of the RO_2 radicals.

$$\begin{array}{lll} HO_2 + RO_2 & \rightarrow ROOH + O_2 & \textbf{(A)} \\ & \rightarrow ROH + O_3 & \textbf{(B)} \\ & \rightarrow OH + RO + O_2 & \textbf{(C)} \end{array}$$

Carbonyl containing RO_2 radicals have previously been believed to pass exclusively through reactions (A) and (B), both radical termination channels.[1] However, recent research has shown that significant OH regeneration, (C), is also possible.[2] The acetyl peroxy radical ($CH_3C(O)O_2$) is of particular importance as it is an isoprene (C_5H_8) oxidation product, the major constituent of biogenic emissions from large forested areas and studies of the title reaction should help to our understanding of isoprene oxidation in low NO_x environments.

The reaction of $CH_3C(O)O_2$ with HO_2 has been studied at 292 and 325 K and at 200 and 760 Torr using $Cl_2/CH_3OH/CH_3CHO$ mixtures in the Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC) at the University of Leeds. Reactants and products of channels (A) and (B) were measured using FTIR spectrometry (Bruker IFS 66) and a commercial O_3 analyser (Thermo 49C) while channel (C) was monitored by direct OH detection using the Fluorescence Assay by Gas Expansion (FAGE) technique.

Figure 1 shows product yields in the first temperature dependent study of the $CH_3C(O)O_2$ + HO_2 reaction. Preliminary results show significant OH yields compared to control experiments. Further modelling and data analysis is required to determine the branching ratio of the reaction which will be presented.

References

(1) H. Niki *et al.*, *J. Phys. Chem.*, **1985**, 89, 588
(2) M. E. Jenkin *et al.*, *Phys. Chem. Chem. Phys.*, **2007**, 9, 3149-3162

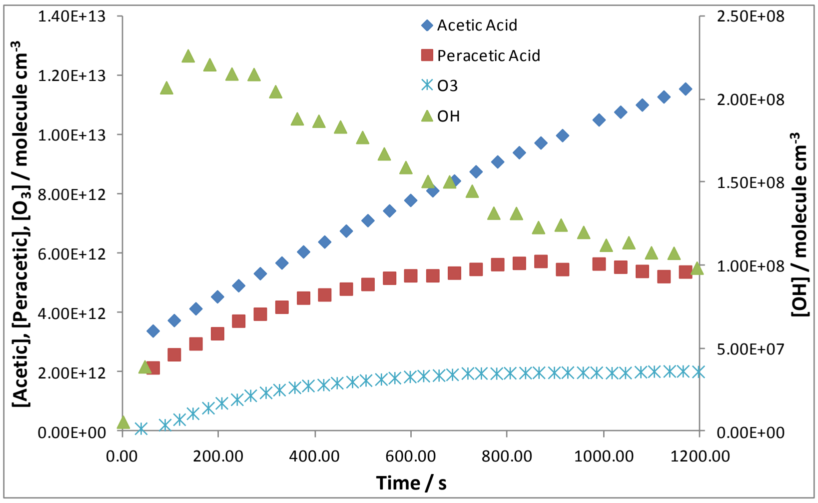


Fig. 1: Acetic Acid, peracetic acid, ozone and OH yields for $CH_3C(O)O_2$ + HO_2 at 760 Torr and 325 K.

Measurements of α–Dicarbonyl Compounds: A Detailed Instrument Intercomparison at the European Photoreactor (EUPHORE)

M. Baeza Romero,[1*] A. Rickard,[2§] S. Peppe,[3] A. Muñoz,[4] S. Ball,[5] M. Ródenas,[4] P. Sánchez,[4] M. Daniels,[5] R. Volkamer,[6] R. Thalman,[6] F. Keutsch[7], S. Henry,[7] P. Monks,[5] I. Goodall,[5] E. Borrás,[4] and M. Vázquez[4]

[1] Universidad de Castilla la Mancha, Spain
[2] National Centre for Atmospheric Science, School of Chemistry, University of Leeds, Leeds, UK
[3] School of Earth and Environment, University of Leeds, UK
[4] Instituto Universitario UMH-CEAM, Spain
[5] Department of Chemistry, University of Leicester, UK
[6] Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, USA
[7] Department of Chemistry, University of Wisconsin, Madison, WI, USA
[§] Now at: National Centre for Atmospheric Science, Department of Chemistry, University of York, York, UK
[*] Corresponding author: mariateresa.baeza@uclm.es

The α-dicarbonyl compounds glyoxal (GLY, CH(O)CHO) and methylglyoxal (MGLY, $CH_3C(O)CHO$)) are ubiquitous intermediates formed in the photo-oxidation of a wide range of anthropogenic and biogenic volatile organic compounds (VOCs). Recent measurements demonstrate that large uncertainties exist in the amount of glyoxal formed from isoprene photooxidation, the dominant VOC emitted into the atmosphere. In addition, α-dicarbonyl compounds are known to be precursors of secondary organic aerosol (SOA), potentially forming a significant fraction of the missing global SOA in atmospheric models. However, the exact role of such compounds in aerosol growth is still not well established. One of the main reasons for such uncertainties is the difficulty in measuring them, as they are very reactive and difficult to handle experimentally.

In order to elucidate both the chemical and instrumental issues related to the quantitative measurement of these compounds, a short experimental chamber campaign was carried out in the EUPHORE photo-reactor in Valencia, Spain to compare a number of currently available techniques (both optical and spectrometric). The campaign comprised a set of experiments simulating typical urban and semi-rural conditions. Measurements were performed over a range of concentrations in order to investigate the impacts of the presence of potential interferants in the chamber gas mixtures sampled (e.g. aerosol, NO_x, short chain carbonyls and ozone). The gas and aerosol phase compositional evolution was monitored simultaneously. Different amounts of GLY and/or MGLY were added directly to the chamber or were generated *in-situ* from the oxidation of various VOC precursors. The following instrumental techniques were employed during the campaign: LED-CE-DOAS (cavity enhanced differential optical absorption spectroscopy), long-path DOAS, SPME (solid phase micro extraction) -GC/MS, FTIR spectroscopy, GC-ECD, BBCEAS (broadband cavity enhanced absorption spectroscopy), LIP (Laser induced phosphorescence), CIR-TOF-MS (chemical ionization time-of-flight mass spectrometry), ATOFMS (aerosol time-of-flight mass spectrometry), FTICR (Fourier transform ion cyclotron resonance mass spectrometry, and LC-MS^n (liquid chromatography-ion trap mass spectrometry).

Experiments were separated into two groups; ***open***, where data was shared between all participants during the execution of the experiments and ***blind***, where the participants share their data only with the referee. We will present an overview of the campaign in terms of participants, instruments, definition of experiments as well as selected results.

Reaction mechanism of the Cl-atom initiated oxidation of 3-methyl-2-butanone and 2,4-dimethyl-3-pentanone

Kennedy K.-T. Vu,[1] Austen Scruggs,[1] Geoffrey S. Tyndall,[2] Samuel Q. Hernandez,[1] John J. Orlando,[2] and Alam S. Hasson[1,*]

[1] California State University, Fresno, CA, USA
[2] National Center for Atmospheric Research (NCAR), Boulder, CO, USA
* Corresponding author: ahasson@csufresno.edu

Carbonyls are important intermediates formed in the atmospheric photo-oxidation of virtually all hydrocarbons. Their subsequent reactions may impact HOx levels and their reaction products may contribute to secondary organic aerosol (SOA) loadings. Reaction with Cl-atoms is an important chemical sink for organics under some conditions, and is widely used in laboratory studies to initiate photochemistry. The atmospheric chemistry of smaller aldehydes and ketones has been well studied, but the dataset for larger (> C4) carbonyls is sparse.

In this work, the mechanisms of the reactions of Cl-atoms with two structurally-related ketones (3-methyl-2-butanone and 2,4-dimethyl-3-pentanone) were investigated. Mixtures containing the ketone, chlorine and air were photolyzed in a reaction chamber at 298 K and 1 atm, and changes in the chemical composition were monitored by long path FTIR spectroscopy and GC-FID. Product yields of formaldehyde, acetone, carbon dioxide and peroxy acyl nitrates (PANs) for both compounds were measured in the presence and absence of NOx or an HO_2 source (methanol). Additional product yield experiments were carried out for the Cl + 3-methyl-2-butanone reaction as a function of O_2 partial pressure.

A partial mechanism for the reactions is shown in Figure 1. Chlorine atoms may abstract a hydrogen atom from either a primary or tertiary carbon center (Reactions R1a and R1b, respectively). The product yields measured imply branching ratios of $Y_{R1a} = Y_{R1b} = 0.5$ for both reactions. The resultant organic peroxy radicals may react to form a hydroperoxide (Reactions R2a and R3a) or an alkoxy radical and OH (Reactions R2b and R3b) in the presence of HO_2. Product yields measured in experiments with an HO_2 source are consistent with a significant fraction of radical recycling via Reactions R2b and R3b. Implications of these measurements will be discussed.

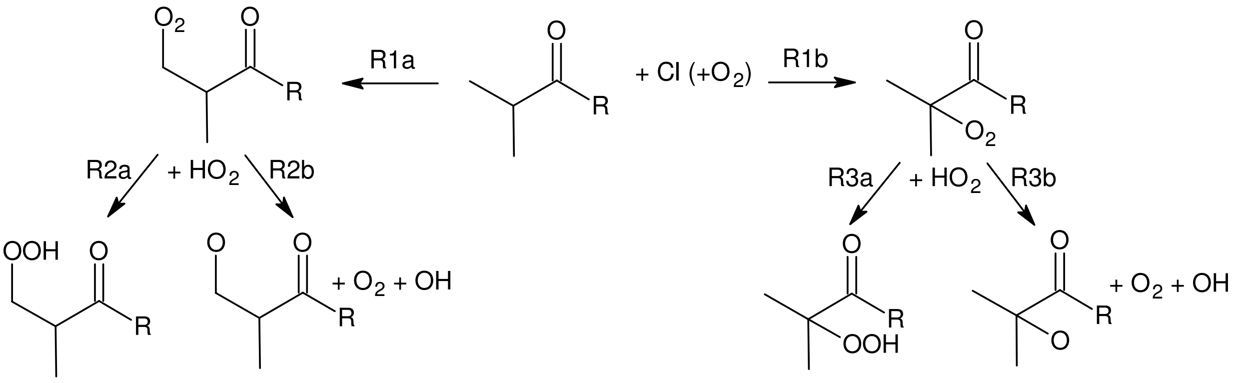


Figure 1. Partial mechanism of the reaction of 3-methyl-2-butanone ($R = CH_3$) and 2,4-dimethyl-3-pentanone ($R = CH(CH_3)_2$) with Cl atoms in air.

Experimental and theoretical investigations for the gas-phase reactions of OH radical with α-pinene and β-pinene.

Manas Ranjan Dash, and **B Rajakumar**[*]
Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India
* Corresponding author: rajakumar@iitm.ac.in

OH radicals play an important role in the chemistry of biologically emitted volatile hydrocarbons in the troposphere. α-pinene and β-pinene are the two most abundant monoterpenes emitted in to the troposphere by coniferous trees.[1] The rate coefficients for the gas-phase reactions of OH radicals with α-pinene and β-pinene have been determined at 298 K and 800 Torr of N_2 using the relative rate method, with propylene as a reference compound. The OH radicals were generated by UV photolysis of hydrogen peroxide (H_2O_2) at 254 nm. A gas chromatograph equipped with a flame ionization detector (GC-FID) was used for quantitative analysis of the reactants. To gain a deeper insight into the reaction mechanism theoretical calculations were also carried out for these reactions. The rate coefficients of OH radical with α-pinene and β-pinene were computed using conventional transition state theory (CTST) coupled meta-hybrid density functional theory (DFT).[2] Structures of the reactants, transition states and products were optimized at M06-2X/6-31G* and M06-2X/6-311++G** level of theories. Energies are obtained by single-point calculation at the above structures using M06-2X/Aug-cc-pVTZ to produce the potential energy surface. Both addition and abstraction channels were explored elaborately. The theoretically computed rate coefficients were compared with experimental results. The OH-driven atmospheric lifetimes of α-pinene and β-pinene were calculated using both experimentally and theoretically determined rate coefficients.

References

(1) Guenther, A.; Hewitt, C. N.; Erickson, D.; Fall, R.; Geron, C.; Graedel, T.; Harley, P.; Klinger, L.; Lerdau, M.; McKay, W. A.; Pierce, T.; Scholes, B.; Steinbrecher, R.; Tallamraju, R.; Taylor, J.; Zimmerman, P. A. *J. Geophys. Res.* **1995**, *100*, 8873-8892.
(2) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215.

Acid-yield measurements and product studies of gas phase ozonolysis of ethene and isoprene as a function of humidity

Mohamed B. Ghalaieny,[1] Kimberley E. Leather[1], Asan Bacak[1], Dudley E. Shallcross[2] and Carl J. Percival[1]
[1]School of Earth, Atmospheric and Environmental Sciences, The University of Manchester, Williamson Building, Oxford Road, Manchester M13 9PL, UK
[2]School of Chemistry, University of Bristol, Bristol BS8 1TS, UK.
* Corresponding author: carl.percival@manchester.ac.uk

Non-methane hydrocarbons (NMHCs) form an important trace component of the atmosphere and are of particular environmental interest because of their deleterious effects on air quality, Earth's climate system and their semiochemical roles in ecosystems. NMHCs are also important precursors to the formation of secondary organic aerosol (*e.g.* Kavouras *et al.*, 1999). The ozonolysis reactions of olefins represent an important source of carboxylic acids. Although the gas phase acid concentrations are small, they are thought to be key species in SOA formation as a result of their low volatility (*e.g.* Ma *et al.*, 2009). Despite this, factors controlling acid formation are not well understood. Both field and modelling studies have encountered difficulties in determining sources of the high concentrations of carboxylic acids that are observed in the atmosphere. Ethene and isoprene are the two most abundant biogenic NMHCs in the atmosphere; therefore measuring acid-yields from the ozonolysis of these two compounds is instrumental in understanding the *in situ* production of carboxylic acids in the atmosphere.

Gas-phase ozonolysis experiments were conducted at room temperature to determine formic acid yields as a function of relative humidity (RH) using the integrated EXTreme RAnge chamber-Chemical Ionisation Mass Spectrometry technique, employing. RHs studied for the ethene system were < 1, 11, 21, 27, 30 % and formic acid yields of (0.07 ± 0.01) and (0.41 ± 0.07) were determined at < 1 % RH and 30 % RH respectively, showing a strong water dependence. RHs studied for the isoprene system were < 1, 10, 25, 30, 45 % and formic acid yields of (0.07 ± 0.01), (0.1 ± 0.01), (0.15 ± 0.03), (0.17 ± 0.02) and (0.18 ± 0.02) were determined respectively, as shown in figure 1. It has been possible to estimate the ratio of the rate coefficient for the reaction of the Criegee biradical, CH_2OO with water compared with decomposition. This analysis suggests that the rate of reaction with water ranges between $1\times10^{-12} - 1 \times 10^{-15}$ cm^3 $molecule^{-1}$ $s^{-1}$and will therefore dominate its loss with respect to bimolecular processes in the atmosphere. Global model integrations suggest that this reaction between CH_2OO and water may dominate the production of HC(O)OH in the atmosphere.

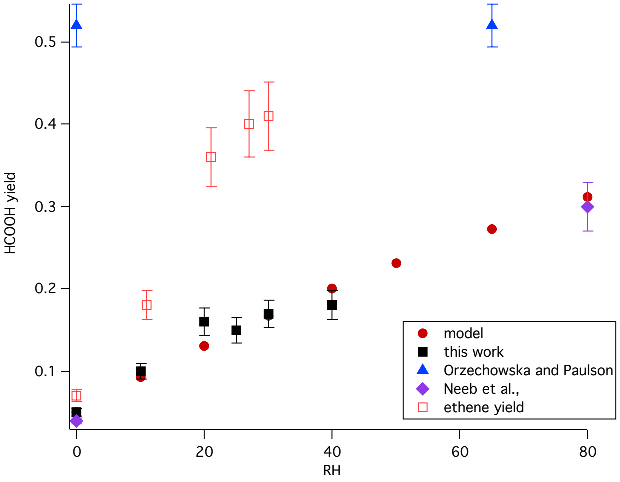


Figure 1 Measured and modelled yields of formic acid from isoprene and ethene ozonoloysis

References

Calvert, *et al.*, *Atmos. Environ.* **1978**, 12, 197.
Kavouras *et al.*, Environ. Sci. Technol. **1999**, 33, 1028.
Orzechowska *et al.*, *J.Phys. Chem.* A **2005**, 109, 5358.
Ma *et al.*, *PCCP*, **2009**, 21, 4184.

Investigation of realistic long term isoprene atmospheric photooxidation in simulation chamber

L.Brégonzio[1*], J.F. Doussin[1], E. Pangui[1], A. Monod[2], F. Siekmann[2], B.Temime[2], M. Camredon[1], B. Aumont[1]

[1] Laboratoire Inter-Universitaire des Systèmes Atmosphériques (LISA UMR 7583), Université Paris Est Créteil-Val de Marne, Université Paris Diderot, 61 Avenue du Général de Gaulle, 94010 Créteil, France
[2] Laboratoire Chimie Provence, Université de Provence, 3 place Victor Hugo, 13331 Marseille, France
* Corresponding author: lola.bregonzio@lisa.u-pec.fr

Isoprene (2-methyl-1,3-butadiene, C_5H_8) is one of the most abundant non-methane hydrocarbons emitted into the troposphere. Its annual global emission has recently been estimated in the range of 440 to 660 TgC (1). Because of its large concentrations and high reactivity with the hydroxyl radical (OH), isoprene can have a strong influence on tropospheric photochemistry. It has been determined recently that isoprene also plays a role in secondary organic aerosol (SOA) formation in the ambient atmosphere even if isoprene leads to low SOA yields. The aim of the present work was to study isoprene photooxidation with OH radical in order to investigate its oxidation products and resulting aerosol production. A special care was taken to the realism of the experiment: light source, NOx level, OH source and aging time (around 10 hours).

To do so, experiments were performed in CESAM chamber at LISA, specifically designed to investigate multiphase processes with a highly realistic irradiation compared to solar radiation (2). Connected to the chamber, a large panel of instruments was used to monitor the gas-phase and the particulate phase during experiments. Gas-phase composition was analysed in-situ via a Fourier Transform Infrared Spectrometer (FTIR) and a Proton Transfer Reaction Mass Spectrometer (PTR-TOF-MS) as well as NO_x and O_3 analyzers. A Scanning Mobility Particle Sizer (SMPS, diameter range 20-800 nm) measured SOA size distributions and total concentrations inside the chamber. An Aerodyne aerosol mass spectrometer (TOF-AMS) was also used to investigate aerosol composition. In each experiment, around 500 ppb of isoprene was injected in the chamber before irradiation. During all the experiment, a very low continuous flow of NO was injected in order to mimic atmospheric emission and maintain oxidation rate, thanks to its propagating role. It therefore allowed us to investigate not only isoprene chemistry but also the fate of its products. Some experiments were carried out with initial ammonium sulfate seed aerosols.

The major gas-phase oxidation products of isoprene we measured, in low NO conditions, are formaldehyde, methacrolein and methyl vinyl ketone identified as first-generation products, and also methylglyoxal and peroxyacyl nitrates (PAN and MPAN), identified as second-generation products. NO_2 to NO ratios, yields of all measured oxidation products and carbon budget were calculated. In all experiments, we noted a SOA production at the end of isoprene oxidation i.e. exhibiting a clear secondary products type growth. The gas-phase composition as well as the aerosol yields obtained during these experiments have been compared to results simulated by an explicit 0D photochemical box model (including around 20000 reactions). The goal of this work was to assess whether or not the processes contained in current chemical mechanisms enable to reproduce observations in the gas-phase.

References

(1) Guenther, A.; Karl, T.; Harley, P.; Wiedinmyer, C.; Palmer, P. I.; Geron C. *Atmospheric Chemical Physics* **2006**, 6, 3181–3210.
(2) Wang, J.; Doussin, J. F.; Perrier, S.; Perraudin, E.; Katrib, Y.; Pangui, E.; Picquet-Varrault, B. *Atmospheric Measurement Techniques* **2011**, 4, 2465-2494.

Kinetic and mechanistic studies of the atmospheric chemistry of isoprene-4,1-hydroxynitrate

Laxmi R. Addala,[1] Geoffrey S. Tyndall,[2] John J. Orlando,[2] Santanu Maitra,[1] Kennedy K.-T. Vu,[1] Austen Scruggs,[1] Lucien Nana,[1] Catalina Olea,[1] Jeffrey Jackson,[1] and Alam S. Hasson[1,*]

[1] California State University, Fresno, CA, USA
[2] National Center for Atmospheric Research (NCAR), Boulder, CO, USA
* Corresponding author: ahasson@csufresno.edu

Isoprene hydroxynitrates are intermediates generated in both the OH and NO_3 initiated oxidation of isoprene. Laboratory measurements suggest that the subsequent reactions of these compounds may be responsible for a substantial amount of the secondary organic aerosol (SOA) generated in the NO_3 + isoprene reaction [1]. This chemistry may also have a significant impact on NOx levels.

In this work, isoprene-4,1-hydroxynitrate was synthesized and its gas phase reactions with OH and Cl were studied in a photochemical reactor with analysis by long path FTIR spectroscopy and GC-FID. Mixtures containing the isoprene hydroxynitrate, air, and either chlorine or methyl nitrite and nitric oxide were photolyzed at room temperature and 1 atm. The rate coefficients for the reactions of isoprene-4,1-hydroxynitrate with OH and Cl were investigated using the relative rate technique using propene, 2-methyl-2-butene and 1-pentene as the reference compounds. Yields of formaldehyde and hydroxyacetaldehyde were also measured from the reaction between OH and isoprene-4,1-hydroxynitrate.

The measured rate coefficients for the reaction of OH and Cl with isoprene-4,1-hydroxynitrate are $(3.7\pm0.4) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} and $(5.1\pm0.5) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}, respectively. The rate coefficient for reaction with OH is significantly lower than the indirect measurement reported by Paulot et al [1]. There are no previous measurements of the Cl + isoprene-4,1-hydroxynitrate rate coefficient for comparison. Product yields measured in the OH-initiated reaction are $Y_{Formaldehyde} = 0.88$ and $Y_{Hydroxyacetaldehyde} < 0.10$. The mechanistic implications of these measurements will be discussed.

References

(1) Paulot, F.; Crounse, J. D.; Kjaergaard, H. G.; Kroll, J. H.; Seinfeld, J. H.; Wennberg, P. O., *Atmos. Chem. Phys.* **2009,** *9*, 1479-1501.

Temperature Dependent formation of glyoxal and methyl glyoxal from the oxidation of isoprene under zero and high NO_x conditions

Ryan Thalman,[1,2] Saewung Kim,[3] John Orlando,[3] Geoff Tyndall,[3] Eleanor Waxman,[1] and Rainer Volkamer[1,2,*]

[1] University of Colorado, Boulder, CO, USA
[2] Cooperative Institute for Research in the Environmental Sciences (CIRES), Boulder, CO, USA
[3] National Center for Atmospheric Research (NCAR), Boulder, CO, USA
* Corresponding author: Rainer.Volkamer@Colorado.edu

Isoprene emitted from the biosphere is the largest single atmospheric source of volatile organic compounds (VOC), contributing 410 Tg annually (about 40% of the global VOC source).[1] Especially in biogenic dominated regions, even small percentage yields of isoprene oxidation products can have significant effects on atmospheric gas and aerosol phase composition. Two alpha-dicarbonyls, glyoxal and methyl glyoxal, have been shown to have multi-generational yields from isoprene oxidation. The magnitude of these yields have been the subject of several recent studies,[2,3,4] that show glyoxal and methyl glyoxal are formed as first generation products, as well as second and third generation products. The first generation yields significantly add to the global source for glyoxal and methyl glyoxal. In this study we present first results regarding the temperature dependence of first generation yields of glyoxal and methyl glyoxal under zero and high NO_x conditions. Experiments combine the atmospheric simulation chamber at the National Center for Atmospheric Research with the CU Light Emitting Diode Cavity Enhanced Differential Optical Absorption Spectroscopy (CU LED-CE-DOAS) for the detection of glyoxal and methyl glyoxal; as well as Proton Transfer Mass Spectrometry for the detection of other isoprene oxidation products. The implications of our results are discussed in context of the inability of current models to explain satellite observations in the mid-latitude biogenic 'hotspot' regions[5,6].

References

(1) Guenther, A.; Karl, T.; Harley, P.; Wiedinmyer, C.; Palmer, P. I.; Geron, C. *Atmos. Chem. Phys.*, **2006**, 6, 3181-3210, doi:10.5194/acp-6-3181-2006.
(2) Volkamer, R.; Barnes, I.; Platt, U.; Molina, L. T.; and Molina, M. J. in: Environmental Simulation Chambers: Application to Atmospheric Chemical Processes, edited by: Barnes, I. and Rudinski, J., 62, Springer, Dordrecht, Netherlands, **2006**.
(3) Paulot, F.; Crounse, J. D.; Kjaergaard, H. G.; Kroll, J. H.; Seinfeld, J. H.; Wennberg, P. O. *Atmos. Chem. Phys.*,**2009**, 9, 1479-1501, doi:10.5194/acp-9-1479-2009.
(4) Galloway, M. M.; Huisman, A. J.; Yee, L. D.; Chan, A. W. H.; Loza, C. L.; Seinfeld, J. H.; Keutsch, F. N. *Atmos. Chem. Phys.*, **2011**, 11, 10779-10790, doi:10.5194/acp-11-10779-2011.
(5) Myriokefalitakis, S.; Vrekoussis, M.; Tsigaridis, K.; Wittrock, F.; Richter, A.; Brühl, C.; Volkamer, R.; Burrows, J. P.; Kanakidou, M. *Atmos. Chem. Phys.*, 2008, 8, 4965–4981, doi:10.5194/acp-8-4965-2008.
(6) Stavrakou, T.; Müller, J.-F.; De Smedt, I.; Van Roozendael, M.; Kanakidou, M.; Vrekoussis, M.; Wittrock, F.; Richter, A.; Burrows, J. P. *Atmos. Chem. Phys.*,**2009**, 9, 8431-8446, doi:10.5194/acp-9-8431-2009.

Alpha-oxoketenes from HPALDs efficiently convert HO_2 into OH radicals in isoprene oxidation

Jozef Peeters,[1,*] Son Vinh Nguyen,[1] Thanh Lam Nguyen,[2] Trissevgeni Stravrakou[3] and Jean-François Müller[3]

[1] University of Leuven, Heverlee, Belgium
[2] The University of Texas at Austin, Austin, TX, USA
[3] Belgian Institute for Space Aeronomy (BISA), Brussels, Belgium
[*] Corresponding author: Jozef.Peeters@chem.kuleuven.be

4-Hydroperoxy-2/3-methyl-but-2-enals (HPALDs) have been predicted to be produced by 1,6-H shift isomerisation of Z-δ-hydroxy-isoprenylperoxy radicals in the atmospheric oxidation of isoprene by OH at low NO.[1,2] They have recently been observed and recognized as important intermediates in isoprene oxidation,[3] although the peroxy isomerisation rate and HPALD yield as well as the contribution to OH recycling still remain very uncertain.[3,4,5] The HPALD formation and subsequent photochemistry involving very fast photolysis processes have been proposed to result overall in 2 HO_2 and up to 3 OH radicals, with α-oxoketenes as main products.[2] On the other hand, recent modeling studies suggest that the very high OH observed in isoprene-rich areas could be explained (partly) by unknown compounds reacting fast with HO_2 and converting it into OH.[6,7] However, at present no VOCs or OVOCs are known to react fast with HO_2.
In this work, the reactions of HO_2 with the α-oxo-ketenes from the HPALDs have been investigated theoretically. The potential energy surfaces, established using suitable DFT/ab initio methods, reveal that HO_2 adds to the α-oxo-ketenes in a three-step process over submerged transition states, forming a peroxy radical. The theoretically estimated rate constants are sufficiently high that reaction with HO_2 should be the predominant removal route of the oxo-ketenes in the conditions of interest. The straightforward subsequent chemistry of the peroxy product is expected to result partly in the removal of a second HO_2, and to yield overall 1 to 2 OH radicals, with methylglyoxal, CO_2, CO, and acetylperoxy radical as main co-products. Modeling results, using the IMAGES CTM, are presented on the impact of these reactions on OH recycling and HO_2 levels in isoprene-rich areas for various scenarios regarding the isoprene-peroxy isomerisation rates and the yields of the HPALDs and their α-oxoketene products.

References

(1) Peeters, J.; Nguyen,T.L.; Vereecken, L. *Phys. Chem. Chem. Phys*. **2009**, 11, 5935-5939.
(2) Peeters, J.; Müller, J.-F. *Phys. Chem. Chem. Phys*. **2010**, 12, 14227-14235.
(3) Crounse, J.D.; Paulot, F.; Kjaergaard, H.G.; Wennberg, P.O. *Phys. Chem. Chem. Phys.* **2011**, 13, 13607-13613.
(4)..Stavrakou, T.; Peeters, J.; Müller, J.-F. *Atmos. Chem. Phys.* **2010**, 10, 9863-9878.
(5) Paulot, F.; Henze, D.K.; Wennberg, P.O. *Atmos. Chem. Phys.* **2012,** 12, 1307- 1325.
(6)..(a) Hofzumahaus, A; et al. *Science* **2009**, 324, 1702-1704; (b) Lu, K.D.; et al. *Atmos. Chem. Phys. Discuss.* **2011**, 11, 11311-11378.
(7) Whalley, L.K.; et al. *Atmos. Chem. Phys.* **2011**, 11, 7223-7233.

The Role of Chemical Activation in the OH-initiated Oxidation of Isoprene in the Troposphere

Mark Pfeifle and Matthias Olzmann*

Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany
* Corresponding author: matthias.olzmann@kit.edu

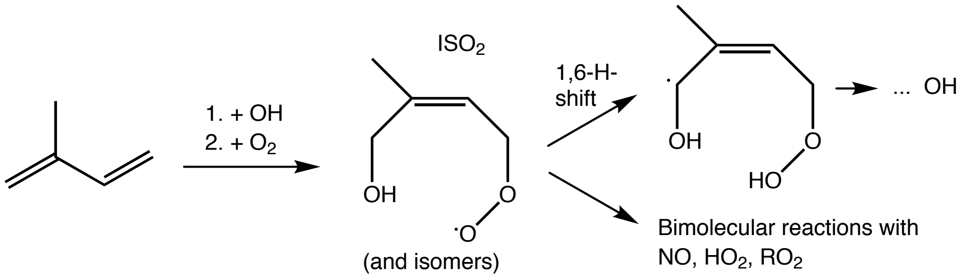
Isoprene is one of the most abundant biogenic hydrocarbons in the atmosphere. Its degradation, initiated by reactive species such as the hydroxyl radical, has been analyzed in numerous studies. While for high NO_x levels the oxidation mechanism is fairly well understood, there are discrepancies for unpolluted environments, where current models underpredict OH concentrations [1]. A reason could be that there are missing OH-regenerating pathways, which compete with the bimolecular sink reactions involving NO. In this context, unimolecular reactions of the hydroxy-peroxy intermediates leading finally to OH were proposed in recent theoretical studies by Nguyen et al.[2] and da Silva et al.[3]. These comprise 1,5-H-shifts of the β-OH-O_2-adducts and 1,6-H-shifts of the δ-OH-O_2-adducts. In Scheme 1, an example for the latter reaction type is given.

It has remained an open question to which degree chemical activation from the exothermic addition steps of OH and O_2 can enhance these unimolecular reaction pathways. Therefore, we studied their kinetics, using master equations with specific rate coefficients from RRKM theory and a simplified statistical adiabatic channel model. Energy profiles were taken from Ref. [2]. One-dimensional tunnelling corrections were applied where necessary, and torsional modes were treated in a one-dimensional hindered rotator approach [4].

In order to account for multiple chemical activation processes, three master equations were coupled [5]. The energy distribution of the OH-isoprene adduct obtained by solving a first master equation was used as input distribution for two further master equations, which describe the unimolecular reactions of the relevant intermediates formed by addition of O_2. As a result, we found no noticeable enhancement of OH-regenerating pathways by chemical activation under atmospheric conditions. Obviously additional pathways have to be considered.

References

(1) Lelieveld, J.; Butler, T. M.; Crowley, J. N.; Dillon, T. J.; Fischer, H.; Ganzeveld, L.; Harder, H.; Lawrence, M.; Martinez, M.; Taraborrelli, D.; Williams, J. *Nature* **2008**, 452, 737-740.
(2) Nguyen, T. L.; Vereecken, L.; Peeters, J. *ChemPhysChem* **2010**, 11, 3996-4001.
(3) da Silva, G.; Graham, C.; Wang, Z.-F. *Environ. Sci. Technol.* **2010**, 44, 250-256.
(4) Hoyermann, K.; Maarfeld, S.; Nacke, F.; Nothdurft, J.; Olzmann, M.; Wehmeyer, J.; Welz, O.; Zeuch, T. *Phys. Chem. Chem. Phys.* **2010**, 12, 8953-8967.
(5) Olzmann, M.; Kraka, E.; Cremer, D.; Gutbrod, R.; Andersson, S. *J. Phys. Chem. A* **1997**, 101, 9421-9429.



Scheme 1. Reaction pathways of the (Z)-δ-OH-O_2-adduct radical formed after subsequent reaction of isoprene with OH and O_2.

Atmospheric Oxidation of Two Isoprene By-Products, Hydroxyacetone and Glycolaldehyde

John J. Orlando,[1*] Geoffrey S. Tyndall,[1] and Domenico Taraborrelli,[2]

[1] Atmospheric Chemistry Division, NCAR Earth System Laboratory, Boulder, CO, USA
[2] Department of Atmospheric Chemistry, Max-Planck-Institute for Chemistry, Mainz, Germany
* Corresponding author: orlando@ucar.edu

Hydroxyacetone [$CH_3C(=O)CH_2OH$, HYAC] and glycolaldehyde [GLYALD, $HOCH_2CH=O$] are common multi-functional oxygenated VOC compounds, formed as first- and second-generation products of isoprene oxidation. Reaction with OH is expected to be the major gas-phase loss for both species, leading to a lifetime of about one (three) day(s) for GLYALD (HYAC). Recent studies by Butkovskaya et al. (1,2) indicate that oxidation of these species by OH might lead to significant yields of formic and acetic acids, particularly at reduced temperature. To confirm these data, we have conducted a study of HYAC and GLYALD oxidation, using traditional environmental chamber / FTIR techniques. Experiments show that organic acid production from HYAC is minimal over a range of temperatures (248-298 K) under the conditions of our experiments. Product yield data for both species over a range of temperatures and conditions, and mechanistic interpretation of the data will be presented.

References

(1) Butkovskaya, N., N. Pouvesle, A. Kukui, Y. J. Mu, and G. Le Bras, *J. Phys. Chem. A* **2006**, 110, 6833-6843.
(2) Butkovskaya, N., N. Pouvesle, A. Kukui, and G. Le Bras, *J. Phys. Chem. A* **2006**, 110, 13492-13499.

Dark reaction of NO_2 with conjugated alkenes

François Bernard,[1,‡] Mathieu Cazaunau,[1] Yujing Mu,[2] Xinming Wang,[3] Véronique Daële,[1] and Abdelwahid Mellouki[1,*]

[1] Institut de Combustion, Aérothermique, Réactivité et Environnement - Centre National de la Recherche Scientifique (ICARE-CNRS), Observatoire des Sciences de l'Univers en région Centre (OSUC), Orléans, France
[2] Research Center for Eco-environmental of Sciences - Chinese Academy of Sciences (RCEES-CAS), Beijing, China
[3] Guangzhou Institute of Geochemistry - Chinese Academy of Sciences (GIG-CAS), Guangzhou, China
[‡] Now at: Guangzhou Institute of Geochemistry - Chinese Academy of Sciences (GIG-CAS), Guangzhou, China
* Corresponding author: mellouki@cnrs-orleans.fr

Nowadays, it is well established that alkenes react preferentially with ozone, OH and NO_3 radicals in the atmosphere (1). However, environmental chamber experiments have shown that NO_2 could contribute significantly to the consumption of some alkenes when using high concentrations of reactants (at ppm level). Previous kinetic measurements showed that the reaction of monoalkenes or non-conjugated alkenes (i.e., α-pinene, 1,4-cyclohexadiene) react slowly with NO_2 in contrast to conjugated alkenes (i.e., α-terpinene, α-phellandrene) (2,3). However, although the reactivity of these compounds through reaction with NO_2 has been demonstrated, the degradation mechanism in gas phase is still poorly defined.

In order to gain further knowledge about the NO_2 chemistry with alkenes, a series of smog chamber experiments have been conducted at ~ 298 K and 760 Torr under dry conditions (RH< 5%). In this study, four alkenes have been selected: isoprene, myrcene, ocimene and 1,3-cyclohexadiene. These species have been chosen according to their emission rates into the atmosphere and their apparent reactivities with NO_2. Reactants (alkenes and NO_2) and oxidation products have been measured by FT-IR spectroscopy. Rate coefficients of NO_2 reaction with the selected alkenes have been determined and found to be as follows (in cm^3 $molecule^{-1}$ s^{-1}): $k(\text{isoprene} + NO_2) = (1.12 \pm 0.09) \times 10^{-19}$; $k(\text{myrcene} + NO_2) = (2.5 \pm 0.1) \times 10^{-19}$; $k(\text{ocimene} + NO_2) = (8.4 \pm 0.6) \times 10^{-19}$ and $k(\text{1,3-cyclohexadiene} + NO_2) = (1.5 \pm 0.1) \times 10^{-18}$. In addition, FT-IR examination of the gas phase mixtures showed that selected alkenes can be divided in two groups: ocimene and myrcene have shown to produce acetone as major identified products whereas isoprene and 1,3-cyclohexadiene lead preferentially to nitrogen-containing products where major IR bands have been assigned to $-NO_2$ and $-O_2\text{-}NO_2$ functional groups.

The reactivity of NO_2 with alkenes will be discussed and tentatively linked to the chemical structure of the studied alkene. The gas phase mechanism leading to the identified oxidation products will be presented and discussed.

References

(1) Atkinson, R.; Arey, J. *Atmos. Environ.* **2003**, 37, S197-S219.
(2) Atkinson, R.; Aschmann, S. M.; Winer A. M.; Pitts, J. N. J. *Int. J. Chem. Kinet.* **1984**, 16, 697-706.
(3) Ohta, T.; Nagura, H.; S. Suzuki, S. *Int. J. Chem. Kinet.* **1986** 18, 1-11.

Kinetic of the gas-phase reactions of a series of alcohols with NO_3 radical

A. Moreno, P. Martín, M.S. Salgado, E. Martínez and B. Cabañas.

Universidad de Castilla-La Mancha, Dpto Química-Física, Facultad de Ciencias Químicas. Av. Camilo José Cela s/n. 13071. Ciudad Real (Spain).

Alcohols are emitted into the atmosphere by a wide number of anthropogenic and natural processes (1). The BVOC that are emitted are mainly isoprene and monoterpenes, but a wide range of other compounds of biogenic origin, including oxygenated compounds, such as aldehydes and alcohols, have been found in the troposphere (2). The alcohols of interest in urban atmospheres are primarily methanol, ethanol and to a lesser extent the C_3 and C_4 species (3). Thus, alcohols have a potential to contribute to the adverse effects that are caused by anthropogenic organic air pollutants, photochemical oxidant formation and haze. The oxidation mechanisms of alcohols produce aldehydes, ketones and organic nitrates as major products (4) in urban areas. The main sources of saturated alcohols are due to their use as motor vehicle fuels, fuel additives and solvent in different industries.

The rate constant for the reaction of NO_3 radical with 2-butanol, 3-methyl-2-butanol and 2,3-dimethyl-2-butanol have been determined using relative kinetic technique in a 50 L glass pyrex photoreactor using in situ FT-IR spectroscopy under room temperature of (298 ± 2) K and in a range of pressure of 350-670 torr and 2-methyl-2-butanol with GC-MS at room temperature and atmospheric pressure. The rate constant measured (in units of cm^3 $molecule^{-1}$ s^{-1}) were $(2.49\pm0.42) \times 10^{-15}$, $(3.04\pm0.51) \times 10^{-15}$, $(2.63\pm0.19) \times 10^{-15}$ and $(1.57\pm0.16) \times 10^{-15}$, respectively. The main reaction channel should be an H-abstraction of the hydrocarbon chain. Thus, 3-methyl-2-butanol, with a C_α-H, has the highest value of rate coefficient. 2-butanol and 2,3-dimethyl-2-butanol have similar rate coefficients and 2-methyl-2-butanol (containing $-CH_2-$ groups) is the lowest reactive. The same trend in reactivity is observed for OH reactions with these alcohols.

The values are also compared with their homologues structural alkanes and discussed. Thus, the substitution of a CH_3 group by an OH group greatly enhances the reactivity of the resulting alcohol, in one magnitude order and a similar trend in reactivity that the observed with alcohols. The dominant atmospheric loss process for these alcohols is their daytime reaction with OH radicals since lifetime is in the range of a few hours. 2-methyl-2-butanol is the compound that remains in the atmosphere longer, and therefore, at night time, NO_3 radicals reaction with this compound should be a relevant process and it could contribute to GWP. MIR index calculations of these compounds indicate that 3-methyl-2-butanol is the most relevant source in ozone generation.

References

(1) König, G.; Brunda, M.; Puxbaum, H.; Hewitt, C.N.; Duckham, S.C.; Rudolph, J. *Atmos. Environ.* **1995**, 29, 861-874.
(2) Noda, J.; Nyman, G.; Langer, S. *J. Phys. Chem. A.* **2002**, 106, 945-951.
(3) Atkinson, R. *Atmos. Environ.* **1990**, 24, 1-41.
(4) Noda, J.; Hallquist, M.; Langer, S.; Ljungström, E. *Phys. Chem. Chem. Phys.* **2000**, 2, 2555-2564.

Nighttime chemistry: Field measurements N2O5 uptake and ClNO2 production

Nicholas L. Wagner[1,2], Theran P. Reidel[3], Trevor C. VandenBoer[4], Cora Young[1,2], Ann M. Middlebrook[1,2], Fatma Ozturk[1], Roya Bahreini[1,2], William P. Dube[1,2], James M. Roberts[1], Joel A. Thornton[3], Steven S Brown[1]

1. Earth System Research Laboratory, NOAA, 325 Broadway, Boulder, Colorado 80305, United States

2. Cooperative Institute for Research in the Environmental Sciences, University of Colorado, UCB 216, Boulder, Colorado 80309, United States

3. Department of Atmospheric Sciences, University of Washington, Seattle, WA 98195, United States

4. University of Toronto

Nighttime chemistry accounts for up to half of the NOx removal from the atmosphere and produces atomic chlorine in the early morning through photolysis of ClNO2. NOx is removed through the production and heterogeneous loss of N2O5. The heterogeneous loss of N2O5 typically produces nitric acid which is removed through deposition. However, it has recently been discovered that in the presence of aerosol chloride, the N2O5 uptake produces ClNO2. The rate N2O5 heterogeneous loss been the subject of several laboratory studies; however, it has rarely been studied using ambient measurements. In this work, N2O5 uptake coefficients are determined from ambient wintertime measurements at the BAO tower in Erie, CO. The uptake coefficients are determined using an iterative box model. These uptake coefficients were found to be anti-correlated with the nitrate fraction of aerosol confirming suppression of uptake by aerosol nitrate. Additionally, a plume of chloride was observed in measurements of aerosol chloride, HCl and ClNO2. The N2O5 uptake coefficient was enhanced in this plume due to the competition between aerosol chloride and nitrate to react with N2O5.

Ozone photo-dissociation - revisited

Shaun A Carl,[1,*] Jozef Peeters,[1] Stijn Vranckx,[2] and Stein Van Bezouw[1]

[1] Department of Chemistry, Celestijnenlaan 200F, Kaltholieke Universieit Leuven, 3001 Leuven, Belgium.
[2] Current address: Shock Wave Lab., RWTH Aachen University, Templergraben 55, 52056 Aachen, Germany
Corresponding author: Shaun.carl@chem.kuleuven.be

We present new, high-resolution determinations of the quantum yield of $O(^1D)$ production, $\Phi(O^1D)_\lambda$, in the photo-dissociation of ozone between 300 nm and 400 nm. $\Phi(O^1D)_\lambda$, is also determined as a function of temperature (200 K to 600 K) between 308 nm and 325 nm over the region associated with the vibrationally-enhanced photodissociation channel leading to $O(^1D) + O_2(a^1\Delta_g)$. Quantum yield determinations at room temperature are extended beyond 325 nm to visible wavelengths over which only the spin-forbidden channel leading to $O(^1D) + O_2(X^3\Sigma_g^-)$ is operative.

The relative yields of $O(^1D)$ and total O (represented by $O(^3P)$ once $O(^1D)$ is quenched) are determined by chemiluminescence of respectively $CF_2(\tilde{A}^1B_1)$ $CF_2(\tilde{a}^3B_1)$ resulting from the reactions of $O(^1D)$ and $O(^3P)$ with C_2F_4. This method proves to be very sensitive towards $O(^1D)$ and $O(^3P)$. Combination of both detection methods provides a highly sensitive technique for determining the $\Phi(O^1D)_\lambda$ of O_3 photolysis; the major advantages are that our technique does not require any external excitation for O-atom detection nor the knowledge of the ozone absorption cross-section, laser energy, or amounts of ozone photolysed.

Accurate $\Phi(O^1D)_\lambda(T)$ determinations were enabled using a specially-designed temperature-graded reaction cell with parallel simultaneous detection of $O(^1D)$ at different sections (temperatures) of the reaction chamber using a series of photomultiplier tubes. The results are compared to the recent *ab initio* quantum mechanical study of the $O(^1D)$ formation in the photolysis of ozone by Grebenshchikov and Rosenwaks [1].

References

(1) Grebenshchikov, S. Y.; Rosenwaks, S. *J. Chem. Phys.* **2010** 114 , 9809-9819.

Field measurements and modelling of OH, HO_2 and OH reactivity in low NO_x environments

Lisa Whalley,[1,2] Trevor Ingham,[1,2] Daniel Stone,[1] Stewart Vaughan,[1] Hannah Bunyan,[1] Ingrid George,[3] Peter Edwards,[4] Mat Evans[5,6] and Dwayne Heard [1,2,*]

[1]School of Chemistry, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK
[2]National Centre for Atmospheric Chemistry, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK
[3]US Environmental Protection Agency, 109 TW Alexander Drive, Durham, NC 27709, USA
[4]ESRL, National Oceanic and Atmospheric Administration, 325 Broadway, Boulder, CO 80305-3328, USA
[5]Department of Chemistry, University of York, York, YO10 5DD, UK
[6]National Centre for Atmospheric Chemistry, University of York, York, YO10 5DD, UK
* Corresponding author: d.e.heard@leeds.ac.uk

The abundance of OH controls the photochemical turnover rate and the lifetimes of trace gases in the atmosphere. Field measured concentrations of OH and HO_2 radicals, and comparison with the results of box model simulations, for example using the detailed *Master Chemical Mechanism*, provide a sensitive test of our understanding of the rates of atmospheric processes. Field measurement of OH reactivity enables quantification of sinks for OH which are not captured in models. This paper will present results and model calculations from recent field experiments in a range of low NO_x environments, namely:

(a) Seasonal OH and HO_2 measurements over a whole year at Cape Verde in the remote Atlantic Ocean (1, 2), where a strong correlation with the rate of ozone photolysis and perturbations from halogen chemistry were observed, (b) Ground and aircraft OH, HO_2 and OH reactivity measurements in and above the Borneo rainforest (3,4), where there are significant missing sources and sinks of OH (Figure 1) and where recycling of OH is needed to give agreement with models (Figure 2), (c) Night-time aircraft measurements over the UK, where significant HO_2 levels were observed, strongly correlating with NO_3 radicals, indicating closely coupled chemistry, and (d) OH and HO_2 measurements in clouds during a hill cap cloud study in Germany, where in cloud HO_2 concentrations could only be modelled successfully if there is heterogeneous processing on the surface of aerosols.

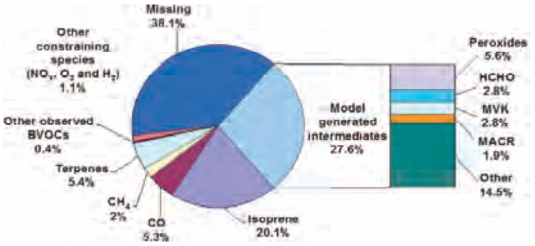


Figure 1. Percentage loss of OH in the Borneo rainforest via reaction with measured sinks and with intermediates calculated by the Master Chemical Mechanism. Note the large fraction of missing reactivity.

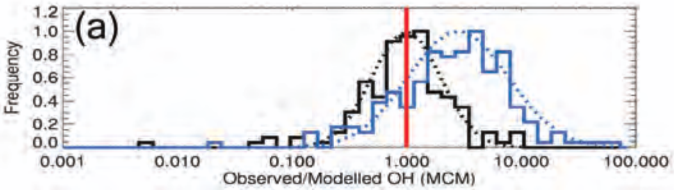


Figure 2. Ratio of measured (BAE146 aircraft) to modeled (MCM) OH concentrations above the Borneo rainforest for isoprene < 15 ppt (black) and for isoprene > 15 ppt (blue). ~ 3 OH molecules need to be recycled in order to bring the modeled OH into line with the measurements (4).

References

(1) Vaughan, S. *et al. Atm. Chem. Phys*. **2012**, 12, 2149-2172.
(2) Whalley, L.K. *et al. Atm. Chem. Phys*. **2010**, 10, 1555-1576.
(3) Whalley, L.K. *et al. Atm. Chem. Phys*. **2011**, 11, 7223-7233.
(4) Stone, D. *et al. Atm. Chem. Phys*. **2011**, 11, 6749-6771.

Interaction of NO_2 with TiO_2 surface under UV irradiation: uptake and products

Atallah El Zein and Yuri Bedjanian*

Institut de Combustion, Aérothermique, Réactivité et Environnement (ICARE), CNRS, Orléans, France
* Corresponding author: yuri.bedjanian@cnrs-orleans.fr

Titanium dioxide, TiO_2, is a very efficient photocatalyst leading to the degradation of organic species under UV irradiation. In addition, TiO_2 is known to transform nitrogen oxides (NO/NO_2), via catalytic heterogeneous reactions, to HNO_3, which remains on the TiO_2 surface. Due to these photocatalytic properties TiO_2 is widely used in a variety of so-called de-polluting building materials aimed to remove the nitrogen oxides from the atmosphere. Titanium dioxide, although being a minor component of mineral dust particles, is believed to be responsible for the photochemical reactivity of atmospheric mineral aerosols. Despite the existence of several experimental studies of the NO_2 reaction with illuminated TiO_2 surface, the quantitative information on its kinetics and products under different atmospheric conditions remains limited, not systematic and sometimes controversial.

In the present work the interaction of NO_2 with TiO_2 solid films was studied under UV irradiation using a low pressure flow reactor (1 – 10 Torr) combined with a modulated molecular beam mass spectrometer for monitoring of the gaseous species involved. The NO_2 to TiO_2 reactive uptake coefficient was measured from the kinetics of NO_2 loss on TiO_2 coated Pyrex rods as a function of NO_2 concentration, irradiance intensity ($J_{NO2} = 0.002 – 0.012\ s^{-1}$), relative humidity (RH = 0.06 – 69 %), temperature (T = 275 – 320 K) and partial pressure of oxygen (0.001 – 3 Torr). The initial uptake coefficient of NO_2 on illuminated TiO_2 surface (with 90 ppb of NO_2 and $J_{NO2} = 0.006\ s^{-1}$) was found to be $\gamma_0 = (1.2 \pm 0.4) \times 10^{-4}$ (calculated using BET surface area) under dry conditions at T = 300 K. The steady state uptake, γ, was several tens of times lower than the initial one, independent of relative humidity, and was found to decrease in the presence of molecular oxygen. In addition, it was shown that γ is not linearly dependent on the photon flux and seems to level off under atmospheric conditions. Finally, the following expression for γ was derived, $\gamma = 2.3 \times 10^{-3} \exp(-1910/T)/(1 + P^{0.36})$ (where P is O_2 pressure in Torr), and recommended for atmospheric applications (for any RH, near 90 ppb of NO_2 and $J_{NO2} = 0.006\ s^{-1}$).

HONO, NO and N_2O were observed as the products of the NO_2 reactive uptake to illuminated TiO_2 surface with the sum of their yields corresponding to nearly 100% of the nitrogen mass balance. The yield of the products was determined as a function of different parameters such as irradiance intensity, relative humidity, temperature, concentrations of NO_2 and O_2. The yield of N_2O was found to be (0.15 ± 0.05) independent of the experimental conditions. The distribution of the products between NO and HONO was found to be independent of temperature in the range T = 280-320 K and was governed by relative humidity: increase in RH led to lower NO and higher HONO yield, with a nearly 65% maximum reached at ~5 % RH. Presence of molecular oxygen was shown to shift the HONO/NO distribution to HONO at low RH (<5%) with no effect at higher RH where HONO yield has its maximum value. The following values for the product yields of the NO_2 interaction with pure TiO_2 under real atmospheric conditions can be recommended from this work: 0.65±0.10, 0.05±0.05 and 0.15±0.05 for HONO, NO and N_2O, respectively. The mechanism of the photoinitiated heterogeneous reaction and possible atmospheric implications of the obtained results will be discussed.

Formation of iodine oxide particles from the photooxidation of CH_3I in the presence of O_3, under the conditions of a major nuclear power plant accident

Zhang S. [1,2], Strekowski R. S. [1], Temime-Roussel B. [1], Bosland L. [2], Wortham H. [1], Vola D.[2], Monod A. [1*]

[1] Aix-Marseille Univ., Marseilles, France
[2] Institut de Radioprotection et de Sûreté Nucléaire, DPAM/SEMIC/LETR, Cadarache, France,
* Corresponding author: Anne.Monod@univ-amu.fr

The potential importance of iodine in tropospheric chemistry was suggested by Chameides and Davis (1) and there is now increasing evidence that chain processes involving reactive halogen radicals, namely I and IO radicals, play an important role in the formation of new particles (2). In addition to atmospheric interest, the reactivity of iodoalkanes, such as CH_3I, has recently gained increased health and safety interest in the nuclear industry in order to better understand chemical processes responsible for the formation of iodine oxides resulting from a major nuclear power plant accident type Fukushima. Among all of the possible released fission products, volatile iodine has the highest radiological health impact, *i.e.*, the isotope ^{131}I is known to bind to the thyroid gland. The quantity of volatile iodine containing compounds that would be released into the environment is, therefore, a major security and public health issue.

We have investigated the photooxidation of CH_3I using UV-C radiation in the presence of ozone and humidity at 30°C in a smog chamber, *i.e*; conditions that are representative of a major nuclear power plant accident in the containement building of the reactor. The size distributions and compositions of the particles were monitored with a SMPS, and a HR-ToF-AMS. The results show that important amounts of particles were formed as soon as CH_3I was injected into the chamber. The particles contained different forms of iodine oxides ($H_xI_yO_z$), and their time profiles were monitored. The influence of irradiation, concentrations of O_3, CH_3I and relative humidity were tested and are discussed. The evolution of the size and composition of the formed particles is of particular interest for the prediction of filtration efficiency in the case of a major nuclear power plant accident.

References

(1) Chameides W. and Davis D., *J. Geophys. Res.*, **1980**, 85, 7383–7398.
(2) Saunder R.W. and Plane J.M.C., *Environ. Chem.*, **2005**, 2, 299-303.

Kinetics of electron attachment to fluorocarbon radicals

Nicholas Shuman,[1] Thomas M. Miller,[1] and A.A. Viggiano[1*]

[1] Air Force Research Laboratory, Space Vehicles Directorate, Kirtland AFB, NM, USA
* Corresponding author: albert.viggiano@us.af.mil

The literature contains almost no experimental data on electron attachment to transient species, such as most radicals. We have recently developed a novel flowing afterglow technique to measure several types of otherwise difficult to study plasma processes, including thermal attachment to radicals.[1] Variable electron and neutral density attachment mass spectrometry (VENDAMS) exploits dissociative electron attachment in a weakly ionized plasma as a radical source. Here, we apply VENDAMS to a series of halocarbon precursors in order to study the kinetics of electron attachment to fluorocarbon radicals. These reactions are of interest as it is known that fluorocarbon radical concentrations affect the efficiency of plasma etching of semiconductor materials, an important industrial process for fabricating microelectronics;[2] however, the kinetics of these processes are entirely undetermined. Thermal electron attachment rate coefficients are measured for CF_2, CF_3, C_2F_5, 1-C_3F_7, 2-C_3F_7, 1-C_3F_5, 2-C_3F_5, and 3-C_3F_5 from 300 to 600 K. The magnitude and temperature dependence of the rate coefficients varies significantly from species to species, as is expected for electron attachment processes, which are highly sensitive to the specifics of the potential surface; however, across all species and conditions, attachment never exceeds 5% of the calculated collisional rate coefficient. The C_2 and C_3 species all attach purely dissociatively to form F^-. CF_2 does not attach electrons to form stable anions. CF_3 attaches both dissociatively and associatively, and rate coefficients for the individual product channels are measured as both a function of temperature and of pressure. The results are fit using a kinetic modeling approach, in which electron attachment is separated as fully as possible into discrete steps and each individual step treated using statistical theory.[3] The modeling reproduces the experimental data exceptionally well, and is used to extrapolate from the results to temperature and pressure conditions inaccessible by the experiment, including to non-thermal plasmas most relevant to plasma processing.

References

(1) Shuman, N. S., Miller, T. M., Friedman, J. F., Viggiano, A. A., Maergoiz, A. I., Troe, J. *J. Chem. Phys.* **2011**, 135, 054306.

(2) Christophorou, L. G., Olthoff, J.K "Fundamental Electron Interactions with Plasma Processing Gases". Kluwer Academic/Plenum Publishers, New York **2004**.

(3) Troe, J.; Nikitin, E. *Mol. Phys.* **2012** in press.

Reactions of Nitrogen-Containing Carbanions in the Gas Phase

Zhibo Yang[1], Callie A. Cole[1], Oscar Martinez, Jr.[1,4], Marshall Y. Carpenter[1], Theodore P. Snow[2,3], and Veronica M. Bierbaum[1,3]

[1] Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309, USA
[2] Department of Astrophysical and Planetary Sciences, University of Colorado, Boulder, CO 80309, USA
[3] Center for Astrophysics and Space Astronomy, University of Colorado, Boulder, CO 80309, USA
[4] Harvard Center for Astrophysics, 60 Garden Street, Cambridge, MA, USA.

A fundamental goal of astrobiology is to discover the origin of life in the universe. An intimate knowledge of the chemical reactions taking place in the interstellar medium (ISM) may contribute more pieces to this complex puzzle. Reactions involving organic molecules are especially important to astrobiology. Several carbon- and nitrogen-containing anions (CN^-, C_3N^-, and C_5N^-) have been spectroscopically detected in the ISM, and this study focuses on the gas phase reactivity of these and related anions with the most abundant atomic interstellar species, hydrogen atom. The tandem flowing afterglow-selected ion flow tube (FA-SIFT)[1] was used to experimentally determine the rate constants and products of these reactions. C_nN^- (n = 1-6), $C_nN_2^-$ (n = 1, 3, 4, 5), and $C_nN_3^-$ (n = 2, 4) were formed by discharge from a graphite rod in the presence of N_2, and were thermalized in helium buffer gas. Reagent ions were then mass-selected using a quadrupole mass filter before entering the reaction flow tube. Hydrogen atoms were formed by the thermal dissociation of H_2, and subsequently introduced into the flow tube. A second quadrupole mass filter coupled to an electron multiplier was used to detect the reaction products, and the observed reaction efficiencies are reported in the attached figure. Theoretical calculations at the B3LYP/aug-cc-pVTZ level of theory were conducted to further understand the mechanisms of these reactions. In future studies, these anion species will be studied in the context of their reactivity with nitrogen and oxygen atoms. Overall, an exploration of interstellar reactions is integral to answering one of the principal questions raised by astrobiology: the origin of life in the universe.

References

(1) Van Doren, J. M.; Barlow, S. E.; DePuy, C. H.; Bierbaum, V. M. *Int. J. Mass Spectrom.* **1987,** 81, 85-100.

Reactions of the Oxygen Radical Cation

Charles M. Nichols,[1] Zhibo Yang,[1] Benjamin B. Worker,[1] Denver R. Hager,[1] Veronica M. Bierbaum[1,*]

[1] University of Colorado, Boulder, CO, USA
* Corresponding author: Veronica.Bierbaum@colorado.edu

The atomic oxygen cation, O^+, is a highly reactive substance important to atmospheric, interstellar, and, combustion chemistry. In fact, it makes up over 90% of the ionic constituents at low-earth orbit elevations.[1] Despite this abundance, the reactions of this ion have not been studied comprehensively.

The experiments were carried out using the flowing afterglow-selected ion flow tube (FA-SIFT). O^+ is generated by ionization of carbon monoxide gas through use of the electron impact ionizer. The oxygen cations are then mass-selected using a quadrupole mass filter and injected into the reaction flow tube where they are thermalized through collisions with He buffer gas, and allowed to react with molecular reagents introduced downstream in the flow tube. The rate constants are measured by monitoring the decrease of the reactant ion signal using a quadrupole mass filter as a function of reaction distance. Branching ratios are determined by plotting the percentage of product ion distribution against the reaction distance and extrapolating back to zero reaction distance.

A preliminary study of the reactions of O^+ with the methyl halogens, and a series of fully fluorinated compounds has been completed in this lab. Reaction rate constants and branching ratios were experimentally determined for each of the halogenated methanes: CH_3F, CH_3Cl, CH_3Br, and CH_3I. Reactions proceed very fast with efficiency above 50% of the collision rates calculated using parameterized trajectory theory. Trends in branching ratio data show a proclivity for the formation of the methyl cation, CH_3^+. The fluorinated compounds understudy includes CF_4, SF_6, and SF_5CF_3. Although fully fluorinated species are very stable, the high internal energy of the oxygen cation prompted these reactions to occur quickly with rate constants on the order of 10^{-9} cm^3 s^{-1}. For each reaction, the oxygen atom ended up on the neutral species.

Additionally branching ratios and reaction rate constants were determined for the reactions of O^+ with a series of organic compounds. These systems were studied to get an idea for the general reactivity of the cation with different functional organic groups. Reactions of the oxygen cation with acetaldehyde, acetic acid, acetone, benzene, dimethyl either, methanol, methyl formate, and pyridine were characterized through this study. Due to the high internal energy of the oxygen cation, high energy ionic products were observed. Additionally, these reactions occurred quickly and proceeded at collision rate for some species.

References

(1) Li, X.; Huang, Y.-L.; Flesch, G.D.; Ng, C.Y. *J. Chem. Phys.* **1997**, 106(3), 928

Gas-Phase Chemistry of Polycyclic Aromatic Hydrocarbon Anions

Nicholas J. Demarais,[1,*] Zhibo Yang,[1] Oscar Martinez Jr.,[1,4] Nadine Wehres,[1,2]
Theodore P. Snow,[2,3] and Veronica M. Bierbaum[1,2]

[1] Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, USA
[2] Center for Astrophysical and Space Astronomy, University of Colorado, Boulder, CO, USA
[3] Department of Astrophysical and Planetary Sciences, University of Colorado, Boulder, CO, USA
[4] Current Address: Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA
* Corresponding author: Nicholas.Demarais@Colorado.edu

Ion-neutral chemistry is an integral component in determining the evolution of the interstellar medium (ISM). The detection of anions in the ISM in the past decade highlights the importance of their inclusion in models of this environment. The inclusion of polycyclic aromatic hydrocarbons (PAHs) in models of dense clouds has dramatic consequences. However, a problem with including PAH anions in models of interstellar clouds is that very little work has been done. Experimental and computational studies have been carried out to investigate reactions of polycyclic aromatic hydrocarbon anions with H atom and neutral species of interstellar relevance. The rate constants, mechanisms, and products observed provide insight into the chemistry of PAH anions in the ISM.

The experiments were carried out using a flowing afterglow-selected ion flow tube (FA-SIFT) Mass Spectrometer.(1) PAHs were introduced into the gas-phase through their vapor pressure or laser induced acoustic desorption (LIAD).(2) PAH anions were generated by chemical ionization, mass selected by a quadrupole mass filter, and injected into the reaction flow tube. Subsequently, reagent molecules of known concentration were introduced into the reaction flow tube and allowed to react. Hydrogen atoms were produced by thermal dissociation of H_2. Ion signal intensities were measured using a quadrupole mass filter coupled to an electron multiplier. Reaction rates and product distributions were determined by monitoring the ion signal intensity as a function of atom concentration or reaction distance.

Reactions of small dehydrogenated PAH anions were considered in this work due to their stability compared to the parent PAH anions. The gas phase reactivity of phenide with molecules of interstellar relevance has been studied. In addition, reactions of deprotonated naphthalene and anthracene with H atoms were investigated. Reactions of phenide with neutral molecules proceed through multiple mechanisms including proton abstraction, atom abstraction, and S_N2 processes. Reactions of the dehydrogenated PAH anions with hydrogen atom proceed exclusively through an associative detachment channel. The reaction rate constants and branching ratios measured in the current study provide reaction mechanisms and critical parameters for astrochemical modeling.

Ab initio calculations were carried out at the CCSD(T)/aug-cc-pVTZ level of theory for reactions involving open shell species such as molecular oxygen, and B3LYP/aug-cc-pVTZ level of theory for reactions with closed shell species. Theoretical calculations have provided further insight into the measured rate constants, mechanisms, and products.

Lastly, LIAD has been successfully implemented on an FA-SIFT mass spectrometer. Large, non-volatile PAH molecules have been successfully introduced into the gas-phase using the LIAD technique and sufficient ion densities have been attained to probe reactions with natural, interstellar species. These preliminary results will also be presented

Experimental and theoretical studies of PAH anions with interstellar have been instigated. The rate constants measured for these reactions can be included in chemical models to give insight into the evolution of astrophysical environments. In addition, reactions observed can suggest the existence of previously undetected molecules and influence their possible detection the ISM.

Reaction Rates and Branching Ratios of Molecules with Astrophysical Relevance

Nadine Wehres[1,2,*], Callie A. Cole[2], Nicholas J. Demarais[2], Zhibo Yang[2], Veronica M. Bierbaum[1,2] and Theodore P. Snow[1,3]

[1] Center for Astrophysics and Space Astronomy, University of Colorado, Boulder, CO, USA
[2] Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, USA
[3] Department of Astrophysical and Planetary Sciences, University of Colorado, Boulder, CO, USA
* Corresponding author: Nadine.Wehres@colorado.edu

Many organic molecules have been identified in the interstellar medium (ISM).(1,2) Studying molecules in the ISM is important, since they provide information on the local heating and cooling mechanisms and hence determine the physical conditions in their respective environments. The physical conditions can in turn trigger molecule formation, formation of stars and planets, and eventually drive the evolution of a whole galaxy; moreover they are key to our understanding of the formation and evolution of life.

Here, we will focus on methyl formate ($HCOOCH_3$), methanol (CH_3OH) and formic acid ($HCOOH$) which have been identified in the ISM.(3-5) The abundances of methyl formate in some interstellar environments are about $10^{-7} – 10^{-10}$ with respect to molecular hydrogen (H_2). Gas-phase reaction routes have been proposed in order to explain possible formation mechanisms, but most models significantly underestimate the abundance of methyl formate.(6) Inclusion of formation on interstellar grains increases the abundance of methyl formate, but does not disentangle the relative contributions of gas-phase and solid state processes. Thus, it remains unclear whether the current gas-phase models are complete, or instead further reaction pathways must be included to model interstellar gas-phase chemistry.

We will discuss possible gas-phase reaction routes to the formation of methyl formate in the gas-phase, which we have explored using a tandem FA-SIFT instrument (Flowing Afterglow-Selected Ion Flow Tube).(1) In general, the reagent ion (here, protonated methanol) is generated using electron ionization on a mixture of helium buffer gas and methanol. Mass-selection of the ions of interest is achieved by using a quadrupole mass filter, and helium buffer gas is used to thermalize the hot reactant ions. Upon injection into the flowtube, neutral species (here, formic acid) can be added and the ionic products are detected using a second quadrupole mass analyzer in combination with an electron multiplier. Preliminary results indicate the formation of protonated methyl formate from formic acid and protonated methanol as precursor gases. Reaction rates and branching ratios for different pressure and temperature regimes were obtained. We will discuss the results and their implications for astrophysical models.

References

(1) Snow, T.P. and Bierbaum, V.M. *Annu. Rev. Anal. Chem.* **2008**, 1, 229-259.
(2) Herbst, E. and van Dishoeck, E.F. **2009**, *Annu. Rev. Astron. Astrophys.*, 47, 427-480.
(3) Sutton, E.C.; Peng, R.; Danchi, W.C.; Jaminet, P.A.; Sandell, G. and Russell, A.P.G. **1995**, *ApJS*, 97, 455-496.
(4) Cazaux, S.; Tielens, A.G.G.M; Ceccarelli, C.; Castets, A.; Wakelam, V.; Caux, E.; Parise, B. and Teyssier, D. **2003**, *ApJ*, 593, 51-55.
(5) Bottinelli, S.; Ceccarelli, C.; Lefloch, B.; Williams, J. P.; Castets, A.; Caux, E.; Cazaux, S.; Maret, S.; Parise, B. and Tielens, A. G. G. M. **2004**, *ApJ*, 615, 354-358.
(6) Horn, A.; Møllendal, H.; Sekiguchi, O.; Uggerud, E.; Roberts, H.; Herbst, E.; Viggiano, A. and Fridgen, T.D. **2004**, *ApJ*, 611, 605-614.

Cluster Formation and Ion Chemistry in the High Pressure Inlet of a Chemical Ionization Mass Spectrometer: Lessons learned from Field and Laboratory Studies

Stark, H.,[1,2,*] Yatavelli, R. L. N.,[2] Kimmel, J. R.,[1,3] Bertram, T. H.,[4]
Thornton, J. A.,[5] Jimenez, J. L.[2,6]

[1] Aerodyne Research Inc., Billerica, MA, USA
[2] Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO, USA
[3] Tofwerk AG, Thun, Switzerland
[4] Department of Chemistry, University of California San Diego, La Jolla, CA, USA
[5] Department of Atmospheric Sciences, University of Washington, Seattle, WA, USA
[6] Dept. of Chemistry and Biochemistry, University of Colorado, Boulder, CO, USA
* Corresponding author: Harald.Stark@aerodyne.com

We present data on analyte-reagent and reagent-reagent clusters of acetate anion in a high pressure inlet chemical ionization high-resolution time-of-flight mass spectrometer (HRToF-CIMS). We will focus on the ion-molecule reaction dynamics to allow selective measurement of organic acids. Variation of pressures and electric fields in the ion-molecule and cluster dissociation region allowed us to understand reagent ion cluster formation, dynamics and sensitivity of the instrument towards specific compounds. In addition, influence of secondary chemistry after proton transfer to the reagent ion on sensitivity is also explored. Finally, recent field measurements of gas- and particle-phase organic acids in a ponderosa pine forest will be presented.

Excitation function of the channel of collision-induced dissociation in system KJ + Xe

V.M. Azriel[*], L.Yu. Rusin

Institute of Energy Problems of Chemical Physics, Moscow, Russia
[*] Corresponding author: Azriel_Vladimir@mail.ru

Dynamics of dissociation of molecules KJ to ions, induced by collisions with atoms of Xe, is investigated in the range of collision energies from 3 eV to 8 eV by classical trajectory technique. Potential energy surface was built as additive function of three pairwise potentials based on truncated Rittner form [1]. Figure 1 represents the comparison of excitation function calculated from trajectory model with experimental function [2]. One can see good quantitative agreement of both excitation functions in all range of collision energies.

References

(1) Rittner, E.S. *J. Chem. Phys.* **1951**, 19, 1030-1035.
(2) Tully F.P.; Cheung, N.H.; Haberland, H.; Lee, Y.T. *J. Chem. Phys.* **1980**, 73, 4460-4475.

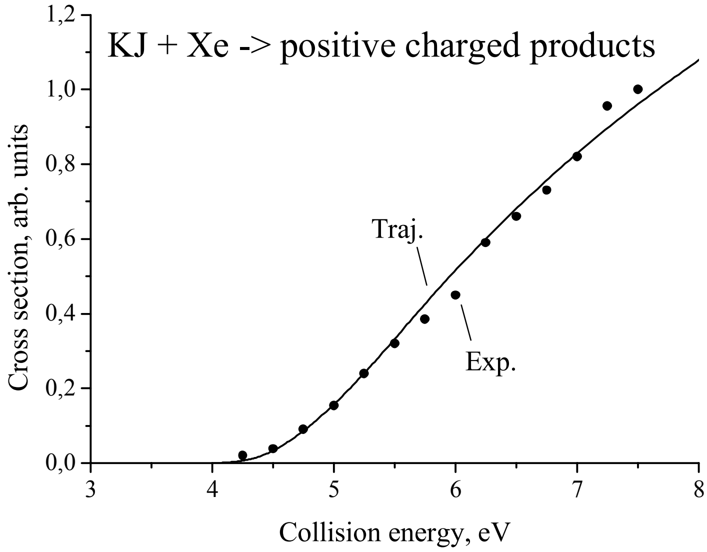


Fig.1. Excitation function of the channel of CID from trajectory calculation (solid line) and experimental data [2] (points).

Semi-Classical TST Calculations of Thermal Rates and KIEs for $H + H_2$, $H + CH_4$ and $CN + H_2$ Reactions

Thanh Lam Nguyen,[1,2,*] John F. Stanton,[1] and John R. Barker,[2]

[1] University of Texas, Austin, TX, USA
[2] University of Michigan, Ann Arbor, MI, USA
* Corresponding author: lnguyen@cm.utexas.edu

Semi-classical transition state theory (SCTST) was developed by W. H. Miller[1] and recently implemented by us using a new algorithm for polyatomic reactions.[2] SCTST in combination with second-order vibrational perturbation theory (VPT2)[3] intrinsically includes fully coupled-anharmonic vibration modes as well as multi-dimensional quantum mechanical tunneling. It has been used to calculate, from first principles, highly accurate thermal rate constants and kinetic isotopic effects (KIE).[4] However, tests on additional reactions are needed to explore its capabilities.

In this work, the microcanonical version of SCTST as implemented in MULTIWELL[5] is used to compute thermal rate constants and KIEs for three reactions, including $H + H_2$, $H + CH_4$, and $CN + H_2$. Potential energy surfaces for these reactions are constructed using the highly accurate HEAT[6] protocol, while rovibrational parameters and anharmonic constants are obtained at CCSD(T)/aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ levels of theory. The *ab initio* calculated results obtained with no adjustments are in excellent agreement with experimental data and with fully quantum dynamic calculations.

References

(1) Miller, W. H. *Faraday Discuss. Chem. Soc.* **1977**, *62*, 40; Miller W. H.; Hernandez R.; Handy, N. C.; Jayatilaka, D.; Willets, A. *Chem. Phys. Lett.* **1990**, *172*, 62;
(2) Nguyen, T. L.; Stanton, J. F; Barker, J. R. *J. Phys. Chem. A* **2010**, *499*, 9.
(3) Mills, I. M. in Rao K. N.; Mathews C. W. (Eds.), Molecular Spectroscopy: Modern Research, Academic Press, New York, 1972, pp. 115-140.
(4) Nguyen, T. L.; Stanton, J. F.; Barker, J. R. *J. Phys. Chem. A* **2011**, *115*, 5118; Barker, J. R.; Nguyen, T. L.; Stanton, J. F. *J. Phys. Chem. A* **2012**, DOI**:** 10.1021/jp212383u.
(5) Barker, J. R. *Int. J. Chem. Kinetics* **2001**, *33*, 232-245; Barker, J. R.; Ortiz, N. F.; Preses, J. M.; Lohr, L. L.; Maranzana, A.; Stimac, P. J.; Nguyen, T. L.; Kumar, T. J. D. MultiWell-2011.3 Software; J. R. Barker, University of Michigan: Ann Arbor, Michigan, USA (http://aoss.engin.umich.edu/multiwell/), 2011.
(6) Tajti, A.; Szalay, P. G.; Csaszar, A. G.; Kallay, M.; Gauss, J.; Valeev, E. F.; Flowers, B. A.; Vazquez, J.; Stanton, J. F. *J. Chem. Phys.* **2004**, *121*, 11599.

Theoretical Investigation of the Hydrogen Abstractions from Furan and its Derivatives by HO_2 and OH Radicals

Harish Kumar Chakravarty, [1,*] Ravi X. Fernandes[1]

[1] Physico Chemical Fundamentals of Combustion, RWTH Aachen University, Templergraben 55, D-52056, Aachen, Germany

* Corresponding author: harish@swl.rwth-aachen.de

The scarcity of fossil fuels in the transportation sector has motivated the interest in search of alternative energy resources. An important alternative is to use biomass derived fuels such as 2-methyltetrahydrofuran as they have a potential to significantly reduce pollutant emissions (1).

Our main objective is to develop detailed chemical kinetic models to predict the combustion behavior of Furan based biofuels in advanced engine such as HCCI. Presently in our group experiments have been performed to measure auto-ignition delay time over wide temperature and pressure range for Furans using shock tube and rapid compression machine. Predictive chemical kinetic models for auto-ignition are developed which demand high accuracy in rate parameters for H-abstraction reactions by OH and HO_2 radicals. The present work focuses on the computational investigation of H abstraction reactions from furans at MP2, G3MP2 and G3B3 level of theories for temperatures between 600-1500 K. Canonical variational transition state theory incorporating Wigner's, Eckart's symmetrical, Eckart's unsymmetrical and small-curvature tunneling corrections has been used in order to estimate accurate Arrhenius parameters for these abstraction reactions. Finally a detailed kinetic model is optimized considering these reactions and validated against experimental results.

References

(1) Andreas, J. J.; Florian, W. K.; Jan, H. B.; Martin, M.; Stefan, P.; Juergen K. *Energy Fuels* **2011**, 25, 4734–4744.

Measurements of α-Dicarbonyl Compounds: A Detailed Instrument Intercomparison at the European Photoreactor (EUPHORE)

M. T. Baeza Romero,[1*] A. Rickard,[2§] S. Peppe,[3] A. Muñoz,[4] S. Ball,[5] M. Ródenas,[4] P. Sánchez,[4] M. Daniels,[5] R. Volkamer,[6] R. Thalman,[6] F. Keutsch[7], S. Henry,[7] P. Monks,[5] I. Goodall,[5] E. Borrás,[4] and M. Vázquez[4]

[1] Escuela de Ingenieria Industrial de Toledo, Universidad de Castilla la Mancha, Spain
[2] National Centre for Atmospheric Science, School of Chemistry, University of Leeds, Leeds, UK
[3] School of Earth and Environment, University of Leeds, Leeds, UK
[4] Instituto Universitario UMH-CEAM, Spain
[5] Department of Chemistry, University of Leicester, Leicester, UK
[6] Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, USA
[7] Department of Chemistry, University of Wisconsin, Madison, WI, USA
[§] Now at: National Centre for Atmospheric Science, Department of Chemistry, University of York, York, UK
* Corresponding author: mariateresa.baeza@uclm.es

The α-dicarbonyl compounds glyoxal (GLY, $CH(O)CHO$) and methylglyoxal (MGLY, $CH_3C(O)CHO$)) are ubiquitous intermediates formed in the photo-oxidation of a wide range of anthropogenic and biogenic volatile organic compounds (VOCs). Recent measurements demonstrate that large uncertainties exist in the amount of glyoxal formed from isoprene photooxidation, the dominant VOC emitted into the atmosphere. In addition, α-dicarbonyl compounds are known to be precursors of secondary organic aerosol (SOA), potentially forming a significant fraction of the missing global SOA in atmospheric models. However, the exact role of such compounds in aerosol growth is still not well established. One of the main reasons for such uncertainties is the difficulty in measuring them, as they are very reactive and difficult to handle experimentally.

In order to elucidate both the chemical and instrumental issues related to the quantitative measurement of these compounds, a short experimental chamber campaign was carried out in the EUPHORE photo-reactor in Valencia, Spain to compare a number of currently available techniques (both optical and spectrometric). The campaign comprised a set of experiments simulating typical urban and semi-rural conditions. Measurements were performed over a range of concentrations in order to investigate the impacts of the presence of potential interferants in the chamber gas mixtures sampled (e.g. aerosol, NO_x, short chain carbonyls and ozone). The gas and aerosol phase compositional evolution was monitored simultaneously. Different amounts of GLY and/or MGLY were added directly to the chamber or were generated *in-situ* from the oxidation of various VOC precursors. The following instrumental techniques were employed during the campaign: LED-CE-DOAS (cavity enhanced differential optical absorption spectroscopy), long-path DOAS, SPME (solid phase micro extraction) -GC/MS, FTIR spectroscopy, GC-ECD, BBCEAS (broadband cavity enhanced absorption spectroscopy), LIP (Laser induced phosphorescence), CIR-TOF-MS (chemical ionization time-of-flight mass spectrometry), ATOFMS (aerosol time-of-flight mass spectrometry), FTICR (Fourier transform ion cyclotron resonance mass spectrometry, and LC-MS^n (liquid chromatography-ion trap mass spectrometry).

Experiments were separated into two groups; ***open***, where data was shared between all participants during the execution of the experiments and ***blind***, where the participants share their data only with the referee. We will present an overview of the campaign in terms of participants, instruments, definition of experiments as well as selected results.

Pressure Dependent HO_2 Calibration of the Fluorescence Assay by Gas Expansion (FAGE) Instrument Using the Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC)

F. Winiberg[1*], S. C. Smith[1,2] and P. W. Seakins[1]
[1] University of Leeds, Leeds, UK;
[2] Now at CIRES, Boulder, Colorado, USA
*Corresponding author: chm5fafw@leeds.ac.uk

The hydroxyl (OH) and hydroperoxy (HO_2) radical are very important tropospheric radical species. The balance between OH and HO_2 (the HO_x cycle) can give understanding of localised atmospheric composition. OH and HO_2 is measured in both ground and aircraft based campaigns using FAGE. Calibration of this non-absolute fluorescence technique is traditionally achieved by H_2O photolysis.[1] Operation of FAGE at varying pressure can affect the instrument sensitivity to HO_x due to internal fluorescence cell pressure changes. These are traditionally accounted by varying the inlet pinhole size of the instrument, however this may alter the gas expansion and hence the instrument sensitivity to OH and HO_2.

Presented here are the initial results from an independent HO_2 pressure dependent calibration method using the stainless steel HIRAC chamber, which can operate at various pressures (0.1 – 1 bar). Formaldehyde, HCHO, is photolysed ($\lambda < 245$ nm) in the presence of O_2 to form $2HO_2$ to steady state, and the post-photolysis HO_2 decay is monitored using FAGE.

The decay is a function of the second order HO_2 self reaction, for which the rate is well known. As $[HO_2] = S_{HO2} \times C_{HO2}$ (FAGE HO_2 signal and instrument sensitivity, respectively), the second order rate equation can be rearranged to give (1) and a plot of $1/S_{HO2}$ vs. time yields C_{HO2} (Fig. 1).

$$\frac{1}{(S_{HO_2})_t} = \frac{1}{(S_{HO_2})_0} + \frac{2k_{HO_2+HO_2}\,t}{C_{HO_2}} \qquad \textbf{(1)}$$

Initial results from both pressure dependent calibrations were good agreement (Fig. 2), validating the widely used traditional “wand” calibration method, supporting field-work and chamber based HO_2 measurements.

References

(1) Faloona *et al.*, *J. Atmos. Chem.*, **2004**, 47, 139-167
(2) R. Atkinson, Atmos. Chem. Phys, **2004**, 4, 1461-1738

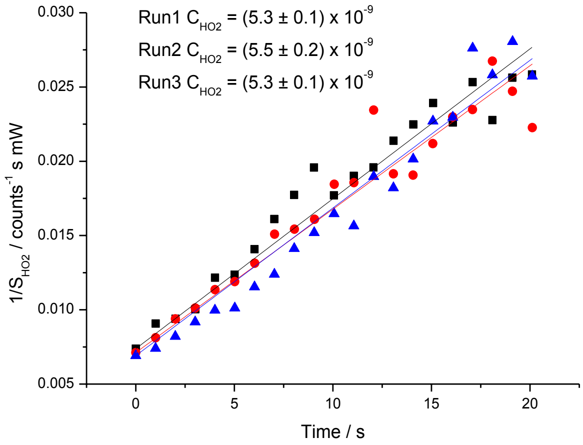


Fig. 1: Second order plot of $1/S_{HO2}$ vs. Time used to determine C_{HO2} ($P_{internal}$ = 1.6 Torr).

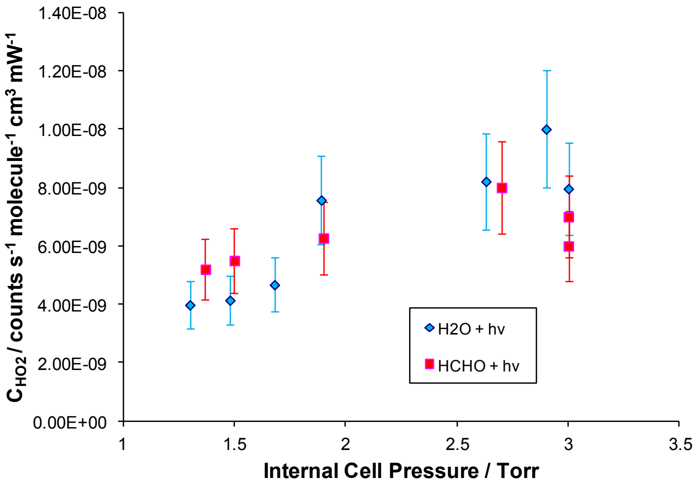


Fig. 2: Comparison of the pressure dependent H_2O photolysis and HCHO photolysis calibration techniques.

Mechanistic Insights into the Tropospheric Ozonolysis of Alkenes: Closed Shell and Radical Product Yields

A. R. Rickard,[1§*] M. S. Alam,[2] M Camredon,[2†] K. P. Wyche,[3] T. Carr,[3]
K. E. Hornsby,[3] P. S. Monks,[3] and W. J. Bloss[2]

[1] National Centre for Atmospheric Science, School of Chemistry, University of Leeds, Leeds, UK
[2] School of Geography, Earth & Environmental Science, University of Birmingham, Birmingham, UK
[3] Department of Chemistry, University of Leicester, Leicester, UK
[§] Now at: National Centre for Atmospheric Science, Department of Chemistry, University of York, York, UK
[†] Now at: LISA, UMR CNRS/INSU 7583, Université Paris Est Créteil et Université Paris Diderot, Paris, France
* Corresponding author: andrew.rickard@york.ac.uk

The gas-phase reaction of alkenes with ozone has been the subject of considerable research interest over several decades owing to its key role in the Earth's tropospheric chemistry. Ozonolysis of alkenes not only leads to removal of hydrocarbons from the atmosphere but also the formation of a wide range of functionalised oxygenated products including carbonyls, organic acids and hydroperoxides, many of which are semi-volatile and can contribute to the formation of secondary organic aerosol [1]. Alkene-ozone reactions are widely recognised as a significant non-photolytic source of OH, HO_2 and RO_2 radicals, initiating further oxidation and contributing to the overall tropospheric HO_x budget, which can be dominant under certain conditions.

We report radical (OH, HO_2 and RO_2) and stable co-product yields for a range of small C_2-C_6 alkenes (ethene – isoprene). Experiments were performed in the European Photoreactor (EUPHORE), using a range of instrumentation including chemical ionisation-reaction time-of-flight mass-spectrometry (CIR-TOF-MS) and laser-induced fluorescence (LIF) to measure stable VOC/oVOCs and radical products respectively [2]. Alkene/ozone reactions were investigated with and without the presence of radical scavengers, in order to suppress side reactions and to obtain reaction rate coefficients, primary/secondary carbonyl and stabilized Criegee intermediate yields. Radical concentrations were measured directly, and interpreted through detailed chemical box modelling drawing upon the Master Chemical Mechanism (MCMv3.2; http://mcm.leeds.ac.uk/MCM) with mechanistic updates from the recent literature and our results.

Directly measured OH yields are found to be broadly in agreement with the existing literature and are entirely consistent with the widely accepted hydroperoxide mechanism. HO_2 yields measured in the absence of an OH scavenger are biased high owing to interference from the decomposition of β-hydroxyalkyl RO_2, formed from the OH + alkene reactions, within the LIF instrument [3]. In the presence of a suitable OH scavenger, the measured HO_2 yields are lower than those inferred in some other recent studies, but in good agreement with those implemented in MCMv3.2 under dry conditions. Mechanistic insights and implications for atmospheric radical levels are also presented.

References

(1) Camredon, M.; Hamilton, J.F.; Alam, M.S.; Wyche, K.P.; Carr, T.; White, I.R.; Monks, P.S.; Rickard, A.R.; Bloss, W.J. Atmos. Chem. Phys., **2010**, 10, 2893-2917.
(2) Alam, M.S.; Camredon, M.; Rickard, A.R.; Carr, T.; Wyche, K.P.; Hornsby, K.E.; Monks, P.S.; Bloss, W.J. *Phys. Chem. Chem. Phys*. **2011**, 13, 11002-11015.
(3) Fuchs, H.B. et al., *Atmos. Meas. Tech.* **2011**, 4, 1209-1225.

Calculation of State-specific Rate Coefficients for Dissociation of $H_2(v, j) + H_2(v', j')$

Margot E. Mandy

Program in Chemistry, The University of Northern British Columbia,
Prince George, British Columbia, CANADA V2N 4Z9

mandy@unbc.ca

State-specific rate coefficients for dissociation of H_2 as the result of collisions with H_2 were calculated for all combinations of *(v, j)* with internal energy below 1 eV. Full dimensional quasiclassical trajectories with the chemically accurate BMKP interaction potential [1] were used with a minimum of 80000 trajectories per energy considered. Although preliminary results had indicated dynamic elevation of threshold, restricted dimensionality trajectories were used to verify that the threshold to dissociation was indeed energetic. Additional large batches of trajectories were used to calculate the cross sections near threshold until the desired precision of the rate coefficient was attained. A piecewise linear excitation function was used to calculate the rate coefficient between 600 and 60000 K, bracketing the range of validity for the interaction potential used.

The resulting state-specific rate coefficients, γ, are parametrized [2] as a function of temperature over the range 1000 - 30000 K.

References

[1] A. I. Boothroyd, P. G. Martin, W. J. Keogh, and M. J. Peterson, J. Chem. Phys., 116 (2002) 666.

[2] M. E. Mandy, and P. G. Martin, J. Chem. Phys. 110 (1999) 7811.

Intrinsic Reactivity and α-effect in Elimination Reactions and Competing Mechanisms in the Gas-phase

Zhibo Yang,[1] John M. Garver,[1,2] Nadine Wehres,[1] Charles M. Nichols,
Benjamin B. Worker,[1,2] Scott Gronert,[3] and Veronica M. Bierbaum[1,*]

[1] University of Colorado, Boulder, CO, USA
[2] United States Air Force Academy, Colorado Springs, CO, USA
[3] Virginia Commonwealth University, Richmond, VA, USA
* Corresponding author: veronica.bierbaum@colorado.edu

Chemical reaction rates are strongly influenced by noncovalent interactions. Gas-phase studies allow the factors inherent to reactants to be revealed in the absence of solvent effects, and the true relationship between the intrinsic character and solvent effects can be understood. One of the most complex areas of interest is the α-effect (the enhanced reactivity relative to a given basicity for nucleophiles with a lone pair of electrons adjacent to the attacking atom). Our current work focuses on the α-effect in the gas-phase reaction of a series of systems to elucidate the nature of the α-effect and to allow these effects to be compared to those in solution. Computational studies are also employed to support discussions of intrinsic differences among anions.

The experiments were carried out using the tandem flowing afterglow-selected ion flow tube (FA-SIFT). Ions were generated by chemical ionization method, and then mass-selected using a quadrupole mass filter and injected into the reaction flow tube. Ions were thermalized through collisions with He buffer gas, and allowed to react with the neutral reagent, which were introduced through multiple inlets along the length of the reaction flow tube. Ionic reactants and products are analyzed in the detection region using a triple-quadrupole mass filter and an electron multiplier. The rate constants, product branching ratios, and reaction efficiencies were obtained. Theoretical calculations were performed to support the experimental studies.

We investigate the reactivity trends and α-effect for a series of reactions in single-channel reaction substrates (tert-butyl chloride and methyl chloride), as well as two competitive reaction systems (dimethyl methylphosphonate and methyl formate). A Brønsted-type correlation is employed to discern differences in reactivity as a function of proton affinity in the E2 reactions of a series of anions with tert-butyl chloride. To refine our assessment of intrinsic differences, we narrowed our focus to reagent pairing of normal and α nucleophiles of nearly identical proton affinity ($FCH_2CH_2O^-$, $PhCH_2O^-$, $(CH_3)_3COO^-$) in the E2 reaction with tert-butyl chloride and the SN2 reaction with methyl chloride. We then expand our reagent pairing (HOO^- versus HO^-, CH_3O^-, $C_2H_5O^-$, and $(CH_3)_2CHO^-$) in the competing reactions of dimethyl methylphosphonate and methyl formate to assess the relationship between product distributions and the magnitude of the α-effect.

While our results do not indicate significant deviations between the α-anions and the normal anions for the E2 mechanism, enhanced nucleophilicity is observed for both $(CH_3)_3COO^-$ and HOO^-. Unlike condensed phase studies, the magnitude of the α-effect in the methyl formate reactions at the sp3 carbon (nucleophilic substitution, S_N2) and the sp^2 carbon (addition-elimination at the carbonyl center, $B_{AC}2$) are nearly identical. The behavior of the α-nucleophiles can be rationalized by "soft" base behavior (in the context of hard and soft acids and bases).

Unusually Fast 1,6-H Shifts of Enolic Hydrogens in Peroxy Radicals: Formation of the First-Generation C_2 and C_3 Carbonyls in the Oxidation of Isoprene

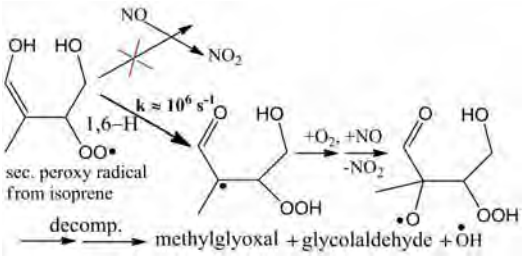
Thanh Lam Nguyen,[2,1] and Jozef Peeters[1,*]

[1] University of Leuven, Heverlee, Belgium
[2] University of Texas at Austin, Austin, TX, USA
* Corresponding author: Jozef.Peeters@chem.kuleuven.be

In a theoretical investigation using the CBS-QB3 // UB3LYP/6-31+G** method supported by higher-level computations such as CBS-QB3 // UQCISD/6-31+G**, the 1,6-H shifts of the enolic hydrogen in peroxy radicals of the type Z-HO-CH=CH-CH_2-$OO^\bullet$ are found to face exceptionally low energy barriers of only about 11 kcal mol^{-1} – *i.e.* 6 to 9 kcal mol^{-1} lower than the barriers for similar shifts of alkanic hydrogens – such that they can proceed at unequaled rates of order 10^5 to 10^6 s^{-1} at ambient temperatures. The unusually low barriers for enolic 1,6-H shifts in peroxy radicals, characterised here for the first, are rationalized. As cases in point, the *secondary* peroxy radicals Z-HO-CH=C(CH_3)-CH($OO^\bullet$)-CH_2OH (Case A) and Z-HO-CH=CH-C(CH_3)($OO^\bullet$)-CH_2OH (Case B) derived from the *primary* Z-δ-hydroxy-peroxy radicals in the oxidation of isoprene, are predicted to undergo 1,6-H shifts of their enolic hydrogens at TST-calculated rates in the range 270 to 320 K of $k(T)_A = 5.4 \times 10^{-4} \times T^{5.04} \times \exp(-1990/T)$ s^{-1} and $k(T)_B = 109 \times T^{3.13} \times \exp(-3420/T)$ s^{-1} respectively, *i.e.* 2.0×10^6 s^{-1} and 6.2×10^4 s^{-1}, respectively, at 298 K, far outrunning in all relevant atmospheric and laboratory conditions their reactions with NO proposed earlier as dominant pathways.[1] These fast enolic-H shifts provide an explanation for the first-generation production of methylglyoxal + glycolaldehyde, and glyoxal + hydroxyacetone in isoprene oxidation at high-NO levels, recently determined by several groups.[2] However, under moderate- and low-NO atmospheric conditions, the fast interconversion and equilibration of the various thermally labile, initial peroxy conformers / isomers from isoprene and the isomerisation of the initial Z-δ-hydroxy-peroxy radicals, both recently proposed by us,[3] are expected to substantially reduce the yields of the small carbonyls at issue.

References

(1) Dibble, T.S. *J. Phys. Chem. A* **2004**, 108, 2199-2207.
(2) Galloway, M.M.; et al. *Atmos. Chem. Phys.*, **2011**, 11, 10779–10790; and references therein
(3) Peeters, J.; Nguyen, T. L.; Vereecken, L. *Phys. Chem. Chem. Phys.* **2009**, 11, 5935–5939.



Novel Reactions in Low Temperature Hydrocarbon Oxidation: A High-Level Computational Investigation of the Kinetics and Thermochemistry of 2-Formyl Ethylhydroperoxide

Amrit Jalan,[1] Ionut M. Alecu,[1] Jorge Aguilera-Iparraguirre,[1] Shamel S. Merchant,[1] and William H. Green[1,*]

[1] Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA
* Corresponding author: whgreen@mit.edu

The reactions of peroxyl radicals derived from fuels comprise a class of important but technically challenging reactions in fuel chemistry. The quantitative understanding of these reactions is essential for accurately modeling and predicting the chemistry that occurs in combustion engines; however, because of the experimental limitations associated with generating and detecting these species and the theoretical challenges with modeling the strongly coupled torsions they possess, the kinetics and thermochemistry of these complex reaction systems is largely unknown. Ketohydroperoxides (HOOQ=O) have long been proposed as important intermediates in low temperature hydrocarbon oxidation.[1] Recent gas phase experiments[2] have corroborated the formation of ketohydroperoxide in low temperature oxidation; however, the formation of products which cannot be readily explained by existing pathways—such as carboxylic acids, ketones, aldehydes, and diketones—was also observed.

Based on evidence obtained over thirty years ago in liquid phase oxidation experiments, we have recently discovered new pathways that lead to the formation of acids and carbonyl compounds starting from the HOOQ=O species. In this work, high-level CCSD(T)-F12/VTZ-F12//M06-2X/MG3S quantum chemistry calculations have been employed to characterize the stationary points along the new reaction pathways using 2-formyl ethylhydroperoxide as a prototypical compound. Conformationally-averaged partition functions for all species were computed using the MS-T method[4] which also accounts for torsional anharmonicity. These were integrated with transition state theory and asymmetric Eckart tunneling coefficients to explore the kinetics of the new reactions. Calculations with other more affordable electronic structure methods were performed to test their applicability in studying similar reactions for larger systems. Results from this effort offer insight into the energetics of the new reactions and on the choice of model chemistry to capture the dominant effects. A more comprehensive study of the newly discovered reaction classes is in progress and will be useful in low temperature oxidation models relevant to combustion, atmospheric and autoxidation chemistry.

References

(1) Zádor, J.; Taatjes, C. A.; Fernandes, R. X. *Progress in Energy and Combustion Science* **2011**, *37*, 371.

(2) Herbinet, O.; Battin-Leclerc, F.; Bax, S.; Gall, H. L.; Glaude, P.-A.; Fournet, R.; Zhou, Z.; Deng, L.; Guo, H.; Xie, M.; Qi, F. *Physical Chemistry Chemical Physics* **2011**, *13*.

(3) Jensen, R. K.; Korcek, S.; Mahoney, L. R.; Zinbo, M. *Journal of the American Chemical Society* **1981**, *103*, 1742.

(4) Zheng, J.; Yu, T.; Papajak, E.; Alecu, I. M.; Mielke, S. L.; Truhlar, D. G. *Physical Chemistry Chemical Physics* **2011**, *13*.

AUTO-IGNITION OF HYDROGEN-OXYGEN-STEAM MIXTURES AT ELEVATED PRESSURES UP TO 74 BAR

Mike Kuznetsov[1,*], Reinhard Redlinger[1], Joachim Grune[2]

[1] Institute for Nuclear and Energy Technologies, Karlsruhe Institute of Technology, Germany
[2] Pro-Science, Ettlingen, Germany
* Corresponding author: kuznetsov@kit.edu

The auto-ignition temperatures of premixed stoichiometric hydrogen-oxygen mixtures diluted with steam were experimentally measured and numerically calculated at the initial pressures from 1 to 74 bar. A series of experiments have been performed in cylindrical geometry for two different scales (23 and 50 mm of inner diameter) and for two different materials: martensitic and austenitic steel. Steam concentration was changed in the range from 0 to 75 mol.%. The experimental procedure for measurements of the auto-ignition temperature consisted of precise pressure and temperature records during the linear pressure and temperature increase with a velocity of 0.1 ^{o}C/s until the self-ignition was identified by a sudden pressure increase associated with an abrupt temperature rise. Initial pressure and temperature of the test gas before heating were kept significantly lower than the expecting self-ignition conditions.

The experimental results continue the well known three explosion limit curve obtained for stoichiometric hydrogen-oxygen mixture up to initial pressure of 1 bar. It was shown that the initial pressure above 1 bar reduces the auto-ignition temperature. For instance, the auto-ignition temperature of 778 K at 2 bar of initial pressure reduces to the temperature of 687 K at pressure of 74 bar. Dilution of the stoichiometric hydrogen-oxygen mixture with up to 75% of steam increases an auto-ignition temperature only in 15-20K depending on the initial pressure. All the tested mixtures at high pressures more than 1 bar are nearby so called third explosion limit where reaction heat release competes with heat losses at the wall surface. Thus, the system becomes sensitive to the size of reaction volume. It was found in current experiments that in two times larger tube the self-ignition temperature decreases in 12-20K compared to the smaller one. Numerical simulation of the auto-ignition for the same mixtures was also performed using several H-O chemical reaction mechanisms: Lutz, Li, Mueller and Maas-Warnatz. Two different numerical codes INSFLA and Cantera have been used for the simulations. As we found in numerical simulations, an induction time of 30-40 s can be used as a threshold for the self-ignition limit. Reduction of the initial temperature corresponding to the induction time of 30-40 s by only 5 degrees completely alters the reactor behavior. The mixture temperature does not change within several hours of residence time. It was shown good agreement of calculated and experimental data on the auto-ignition temperature. Current work was made in order to study explosion limits of stoichiometric hydrogen-oxygen mixtures diluted with steam in order to validate computer codes for safety applications of Boiling Water Reactors at pressures up to 70 bar.

RPMD: A Software Package for Computing Chemical Reaction Rates Using Ring Polymer Molecular Dynamics

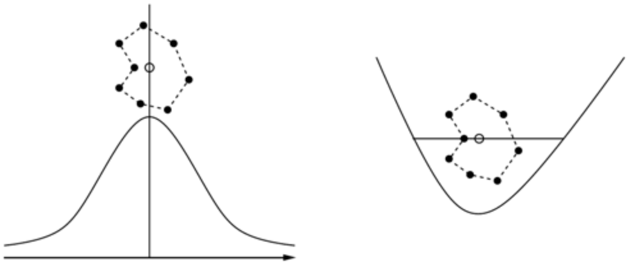
Joshua W. Allen,[1,*] Yury V. Suleimanov,[1,2] and William H. Green[1]

[1] Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA
[2] Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, USA
* Corresponding author: jwallen@mit.edu

Ring polymer molecular dynamics (RPMD) has shown considerable promise as a method for including quantum mechanical (zero-point energy and tunneling) effects in calculations of chemical reaction rates [1-3]. RPMD reaction rate theory exploits the isomorphism between the quantum statistical mechanics of a single particle and the classical statistical mechanics of a fictitious ring polymer; it is essentially a classical rate theory in an extended phase space, and is therefore directly applicable to complex chemical reactions in their full dimensionality.

In this work, we present a new general-purpose software package for the computation of chemical reaction rates for arbitrary gas-phase bimolecular reactions using RPMD simulations [4]. The user supplies an input file describing the reactive system and a function for evaluating the external potential of this system. The specification of the transition state dividing surface – which only affects the rate of convergence of the RPMD simulations, not the final computed rate coefficient – has been generalized to work for a wide variety of reaction families. If no external potential is available, the software can generate a suitable potential via on-the-fly *ab initio* calculations using an external quantum chemistry package. The core of the software is written in Fortran 90, making it very efficient; this is wrapped in a Python layer for a more user-friendly, scriptable interface. The RPMD software is demonstrated for a variety of small-molecule hydrogen abstraction reactions, including systems for which quantum reactive scattering calculations are currently infeasible.

References
(1) Collepardo-Guevara, R.; Suleimanov, Yu. V.; Manolopoulos, D. E. *J. Chem. Phys.* **2009**, 130, 174713.
(2) Suleimanov, Yu. V.; Collepardo-Guevara, R.; Manolopoulos, D. E. *J. Chem. Phys.* **2011**, 134, 044131.
(3) Perez de Tudela, R.; Aoiz, F. J.; Suleimanov, Yu. V.; Manolopoulos, D. E. *J. Phys. Chem. Lett.* **2012**, 3, 493.
(4) Suleimanov, Yu. V.; Allen, J. W.; Green, W. H. **2012**, in preparation.



tunneling

zero-point energy

Fig. 1. Ring-polymer molecular dynamics includes the quantum mechanical effects of tunneling and zero-point energy in calculations of chemical reaction rates.

Nonadiabatic Reactions on Three Coupled PESs of CH_2 and ON_2

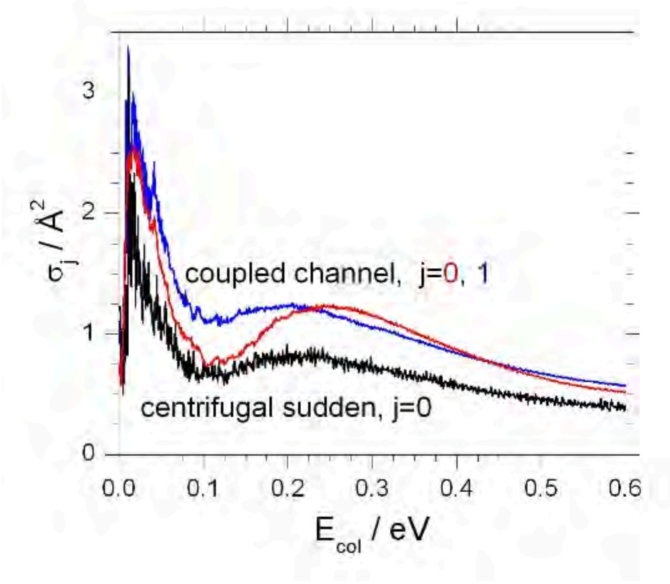
Paolo Defazio,[1] Pablo Gamallo,[2] and Carlo Petrongolo[3,*]

[1] Universita' di Siena, Siena, Italy
[2] Universitat de Barcelona, Barcelona, Spain
[3] Consiglio Nazionale delle Ricerche, Pisa, Italy
* Corresponding author: petrongolo@unisi.it

We present the nonadiabatic collision dynamics and gas kinetics of the combustion and atmospheric reactions $C(^1D) + H_2(X^1\Sigma_g^+) \rightarrow C(^3P) + H_2(X^1\Sigma_g^+)$ / $CH(X^2\Pi) + H(^2S)$ and $O(^1D) + N_2(X^1\Sigma_g^+) \rightarrow O(^3P) + N_2(X^1\Sigma_g^+)$. We use our quantum theory of nonadiabatic effects in triatomics (1,2), the quantum real wavepacket method (3,4), and configuration-interaction PESs, Renner-Teller (RT), and spin-orbit (SO) couplings between the three lowest electronic states of CH_2 and ON_2. We discuss the effects of permutation-inversion symmetry rules and of Coriolis, RT, and SO couplings on reaction probabilities, cross sections, and rate constants. As an example, the figure presents the $O(^1D) + N_2(X^1\Sigma_g^+)$ SO+RT cross sections versus the collision energy, resolved on two N_2 rotational states. We see a resonance-dominated barrierless collision, reflecting the $\tilde{X}^1A'$ deep potential well, and rotational and Coriolis reactivity enhancements, both due to symmetry selection rules. The nonadiabatic interactions play different roles on the quenching dynamics, because the singlet-triplet SO effects are by far more important than the RT triplet ones.

References

(1) Petrongolo, C. *J. Chem. Phys.* **1988**, 89, 1297.
(2) Defazio, P.; Bussery-Honvault, B.; Honvault, P.; Petrongolo, C. *J. Chem. Phys.* **2011**, 135, 144308.
(3) Gray, S. K; Balint-Kurti, G.G.; *J. Chem. Phys.* **1998**, 108, 950.
(4) Meijer, A.J.H.M.; Goldfield, E.M.; Gray, S.K.; Balint-Kurti, G.G. Chem. Phys. Lett. **1998**, 293, 270.



Can Multi-Scale Modeling Accurately "Predict" Molecular Properties? An Illustrative Test for the OH + OH = H_2O + O Reaction

Michael P. Burke,[1*] Stephen J. Klippenstein,[1] Lawrence B. Harding,[1]
and Ahren W. Jasper[2]

[1] Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois 60439, USA
[2] Combustion Research Facility, Sandia National Laboratories, MS 9055, Livermore, CA 94551-0969, USA
* Corresponding author: mpburke@anl.gov

As the power of scientific computing continues to grow, detailed models for complex chemical-transport phenomena play a more significant role in the design process of advanced energy conversion devices (e.g. Ref. 1). As a result, there have been substantial research efforts devoted to the construction and further development of detailed chemical models for conventional and alternative fuels. However, given the enormity of temperature/pressure/bath-gas conditions of potential interest, kinetic models are often used at conditions far outside their validation set, where deficiencies in model performance are observed relatively often. A multi-scale approach to combustion model development has been recently proposed,[2] in which kinetic theory is directly incorporated as a means to ensure a physically meaningful kinetic model and provide reliable extrapolation to engine-relevant conditions. The modeling technique offers complete integration of information from a wide variety of sources – rate constant measurements, global combustion experiments, and *ab initio* theoretical kinetics calculations. The resulting kinetic model consists of a set of theoretical kinetics parameters (with constrained uncertainties), which can be related through kinetics calculations to rate constants (with propagated uncertainties), which can be related through physical models to combustion behavior (with propagated uncertainties). The validity of the approach, and the reliability of extrapolation to new conditions, relies on its ability to properly extract theoretical kinetics parameters from complex information.

In the present work, we evaluate the accuracy of the extracted molecular properties through comparison with high-level *ab initio* electronic structure calculations for the OH+OH = H_2O+O reaction. In the multi-scale modeling, molecular properties for the relevant reactions in H_2O_2 thermal decomposition are optimized against moderate-level *ab initio* electronic structure calculations using standard methods, rate constant measurements, and absorption measurements in shock-heated H_2O_2/Ar mixtures. In the high-level *ab initio* electronic structure calculations, geometries were optimized at the CCSD(T)/cc-pVQZ level and corrections for higher order correlation, core-valence correlation, relativistic, spin-orbit, and diagonal Born-Oppenheimer effects were incorporated. Rovibrational properties of the ground and first excited state were also studied with multi-reference electronic structure methods. Preliminary comparisons between molecular properties from high-level theory and the confidence intervals from multi-scale modeling are promising. Implications for the underlying kinetic and physical models as well as applications to larger systems (where such high-level theory is intractable) are discussed.

References

(1) Hwang, W. Dec, J. Sjöberg, M. *Combust. Flame* **2008**, 154, 387–409.
(2) Burke, M.P.; Klippenstein, S.J.; Harding, L.B. *Proc. Comb. Inst.* **2012**, submitted.

This work was supported by a Director's Postdoctoral Fellowship from Argonne National Lab and by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, under Contract Nos. DE-AC02-06CH11357 and DE-AC04-94-AL85000.

H-migration in Alkylperoxy Radicals in the Atmosphere: Theory-based SAR Development

Luc Vereecken[1]

[1] Max Planck Institute for Chemistry, Mainz, Germany
* Corresponding author: Luc.Vereecken@mpic.de

The fate of alkylperoxy radicals, RO_2, in the troposphere is traditionally thought to be governed by their reactions with HO_2 and RO_2 in pristine conditions, and by NO in polluted areas. H-migration reactions in RO_2 radicals, forming hydroperoxide alkyl radicals, are well-known in combustion where they play an important role in ignition and cool flames, but were considered too slow to contribute to atmospheric chemistry. Recent theoretical studies, however, have proposed a set of alkylperoxy H-migration reactions, predicted to be competitive with traditional RO_2 sinks in the atmosphere. Such H-migrations occur in oxygenated and/or unsaturated alkylperoxy radicals, where the H-migration rate is enhanced by the availability of more weakly bonded hydrogen, e.g. an aldehydic H, an α-OH-substituted hydrogen, or an allylic H. To be effective in the atmosphere, the proposed reactions also need to form hydroperoxide products that do not readily back-migrate the hydrogen, either by have a sizable reverse barrier, or by undergoing facile subsequent rearrangements. The formation of hydroperoxide-substituted compounds through these H-migrations is implied in the regeneration of OH radicals in the VOC oxidation, isoprene in particular, in unpolluted conditions. A particular example of such an OH regeneration mechanism is the Leuven Isoprene Mechanism (1) found in models to yield high quantities of OH, in good agreement with field measurements. The identification of OH-generation reactions in the RO_2 chemistry has been largely driven by theoretical investigations, with very little experimental data available as yet on H-migration in RO_2 radicals in atmospheric conditions. Furthermore, the available experimental data sets seem not always consistent, with theoretical calculations able to reproduce some but not all observations (2). Given the dearth of experimental data, high accuracy of the theoretical predictions is critical.

We describe the impact of the level of quantum chemical theory used in the characterizations of the potential energy surface, and on the predictions of quantum chemical tunneling essential in the description of this reaction class. Furthermore, we work towards the development of a Structure-Activity Relationship for this reaction class, designed specifically for atmospheric conditions and addressing relevant substitutions and H-migration spans. Over 60 H-migrations are examined, covering 1,4- through 1,8-H-migration of primary, secondary and tertiary H-atoms, with oxo-, hydroxy- and unsaturated functionalities at various positions relative to the peroxy group and migrating H-atom. The systematic trends obtained thus are incorporated in a SAR predicting rate coefficients for H-migration.

References

(1) Peeters, J.; Nguyen T.L.; Vereecken L. *Phys. Chem. Chem. Phys.* **2009**, 11, 5935-5939.
(2) Taraborrelli, D.; Lawrence, M.G.; Dillon, T.J.; Gromov, S.; Groß, C.B.M.; Vereecken, L.; Lelieveld, J. *Nature Geosci.* **2012**, 5, 190-193.

Will Water Act as a Photo-catalyst for Cluster Phase Chemical Reactions? Vibrational Overtone Induced Dehydration Reaction of Methanediol

Zeb C. Kramer,[1] Kaito Takahashi, [1,2] Veronica Vaida, [1,3] and Rex T. Skodje[1*]

[1] Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, USA
[2] IAMS, Academia Sinica, Taipei, TAIWAN
[3] CIRES, University of Colorado, Boulder, CO, USA
* Corresponding author: Rex.skodje@colorado.edu

The possibility of water catalysis in the vibrational overtone induced dehydration reaction of methanediol is investigated using *ab initio* dynamical simulations of small methanediol-water clusters. Quantum chemistry calculations employing clusters with one or two water molecules reveal that the barrier to dehydration is lowered by over 20 kcal/mol because of hydrogen-bonding at the transition state. Nevertheless, the simulations of the reaction dynamics following *OH*-stretch excitation show little catalytic effect of water and, in some cases, even show an anticatalytic effect. The quantum yield for the dehydration reaction exhibits a delayed threshold effect where reaction does not occur until the photon energy is far above the barrier energy. Unlike thermally induced reactions, it is argued that competition between reaction and the irreversible dissipation of photon energy may be expected to raise the dynamical threshold for the reaction above the transition state energy. It is concluded that the quantum chemistry calculations of barrier lowering are not sufficient to infer water catalysis in photochemical reactions, which instead require dynamical modeling.

Rate Coefficient for OH Radical Reaction with CO at Low Temperatures

Yingdi Liu and Stanley P. Sander*

Jet Propulsion Laboratory, California Institue of Technology, Pasadena, California 91109
* Corresponding author: stanley.p.sander@jpl.nasa.gov,

The OH radical reaction with CO is of crucial importance in the atmospheres of Mars and Earth. In this work, we measured rate coefficients for the reaction of OH with CO using laser photolysis/laser-induced fluorescence in 150K – 295K temperature range and pressure range 50-900 Torr of different gases diluents. The reaction is studied under pseudo first-order conditions, monitoring the decay of OH by LIF in the presence of a large excess of CO. The observed pressure and temperature dependences is analyzed to derive information about the branching ratio for the addition (HOCO) and disproportionation (H + CO_2) channels.

Accelerated rate coefficients at very low temperatures: OH + ethanol

Rebecca Caravan,[1*] Robin Shannon,[1] Mark Blitz,[1†] Andrew Goddard[1] and Dwayne Heard.[1]

[1] University of Leeds, Leeds, UK [†] NCAS fellow * Corresponding author: cmrlc@leeds.ac.uk

The pulsed Laval nozzle apparatus allows the study of low temperature kinetics under thermally equilibrated conditions. This method coupled with pulsed laser photolysis laser-induced fluorescence (PLP-LIF) has been utilized to study the kinetics of the reaction between OH and ethanol under conditions approaching those of interstellar clouds where both OH and ethanol have been detected. The rate coefficient for OH + ethanol was observed to increase by over an order of magnitude between 295-80 K (Fig. 1). Similar behavior has previously been observed in our studies of OH + acetone and methanol, where a mechanism involving a weakly bound pre-reaction complex has been proposed to explain the strong inverse temperature dependence.[1]

$$\mathrm{OH} + \mathrm{C_2H_5OH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Complex} \xrightarrow{k_2} \mathrm{Products}$$

The complex is bound by ~20 kJ mol^{-1} and is only stabilized at low temperatures. At 150 K, evidence for the role of the complex is substantiated by the observation that the reaction shows a pressure dependence (Fig. 2) which is related to the collisional stabilization of the complex. At 80 K, pressure stabilization of the complex is still evident, however a zero pressure channel is also present which implies the complex proceeds directly to products. A similar bimolecular channel has also been observed for OH + methanol and is rationalized by the occurrence of quantum mechanical tunneling from the complex through the H-abstraction barrier which has been supported theoretically by *ab inito* and MESMER calculations.[2] It is the increased lifetime of the complex at low temperatures that enhances the probability of tunneling through this barrier to products. Previous studies of OH + ethanol show that at room temperature H-abstraction occurs at the weakest bond, which is at the internal CH_2 group.[3] Surprisingly, low temperature studies of the reaction of OH + methanol have shown that quantum mechanical tunneling favours H-abstraction from the alcohol group despite the higher barrier. Enhanced quantum mechanical tunneling via this channel is a result of the higher vibrational frequency associated with breakage to the O-H bond. It is predicted that hydrogen abstraction from ethanol at low temperatures will also proceed via this channel.

References
(1) Shannon, R.J.; Taylor, S.; Goddard, A.; Blitz, M.A.; Heard, D.E.; *Phys. Chem. Chem. Phys*. **2010**, 12, 13511-13514.
(2) Robertson, S.H.; Glowacki, D.R.; Liang, C.-H.; Morley, C.; Pilling, M.J.; MESMER (Master Equation Solver for Multi-Energy Well Reactions), **2008**; an object oriented C++ program for carrying out ME calculations and eigenvalue-eigenvector analysis on arbitrary multiple well systems. http://sourceforge.net/projects/mesmer.
(3) Carr, S.A.; Blitz, M.A.; Seakins, P.W.; *J. Phys. Chem. A*. **2011**, 115(15), 3335-3345.
(4) Wallington, T.J.; Kurylo, M.J.; *Int. J. Chem. Kin.* **1987**, 19(11), 1015-1023.
(5) Hess, W.P.; Tully, F.P.; *Chem. Phys. Lett.* **1988**, 152, 183-189.

Fig. 1 : Temperature dependence of OH + ethanol

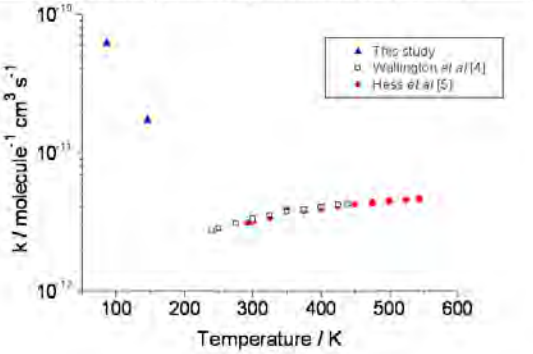
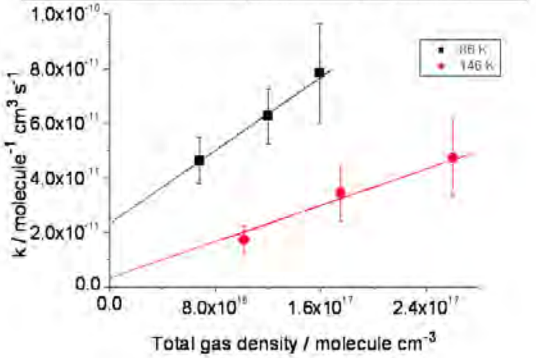


Fig. 2 : Pressure dependence of OH + ethanol



Enhancement of the $NH_2 + NO \rightarrow OH + H + N_2$ Reaction by Vibrational Excitation of NH_2

Nanase Kohno[1], Mari Izumi[1], Hideo Kobayashi[1], Hiroshi Kohguchi[1], and Katsuyoshi Yamasaki[1,*]

[1] Department of Chemistry, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8526, Japan
* Corresponding author: kyam@hiroshima-u.ac.jp

The reaction of amino radical (NH_2) with nitric oxide (NO) has attracted the attention of researchers engaged in atmospheric and combustion chemistry. The fate of NH_2, generated in the atmosphere by $OH + NH_3 \rightarrow NH_2 + H_2O$, is governed by the reaction with the trace species NO, particularly in the urban areas. The $DeNO_x$ process, which is the noncatalytic reduction of NO_x by NH_3 in power plants, is based on the NH_2 + NO reaction. There are three exothermic channels in the reaction of NH_2 with NO:

$$NH_2 + NO \rightarrow OH + H + N_2 \qquad \Delta_r H^\circ_{298} = -24 \text{ kJ mol}^{-1} \qquad (1)$$

$$\rightarrow N_2O + H_2 \qquad \Delta_r H^\circ_{298} = -199 \text{ kJ mol}^{-1} \qquad (2)$$

$$\rightarrow H_2O + N_2 \qquad \Delta_r H^\circ_{298} = -522 \text{ kJ mol}^{-1} \qquad (3)$$

Marcy et al.[1] reported that N_2O via channel 2 is produced from vibrationally excited NH_2 and H_2O in channel 3 is generated by vibrationally relaxed NH_2. In this paper, the authors have studied the effect of vibrational excitation of NH_2 on channel 1.

A gaseous mixture of NH_3(0.5–30 mTorr)/NO(5–100 mTorr)/He(5–100 Torr) in a flow cell at 298 K was irradiated with an ArF laser (193 nm) to initiate NH_2 + NO. $NH_2(\tilde{X}^2B_1)$ and $OH(X^2\Pi, v = 0)$ were detected with laser-induced fluorescence (LIF) via the $\tilde{A}^2A_1 - \tilde{X}^2B_1$ and $A^2\Sigma^+ - X^2\Pi$ transitions, respectively, and H atoms with Lyman-α radiation following two-photon excitation at 243 nm. Time-resolved LIF intensities of the three species were recorded as a function of the delay times between the photolysis and probe lasers under the conditions of various partial pressures. We also have added CF_4 which is an efficient relaxation partner of NH_2 and an inefficient quencher of $OH(A^2\Sigma^+)$, finding the significant reduction of the yield of OH with an increase in CF_4 as shown in Figure 1. The results indicate that channel 1 is enhanced by vibrational excitation of NH_2.

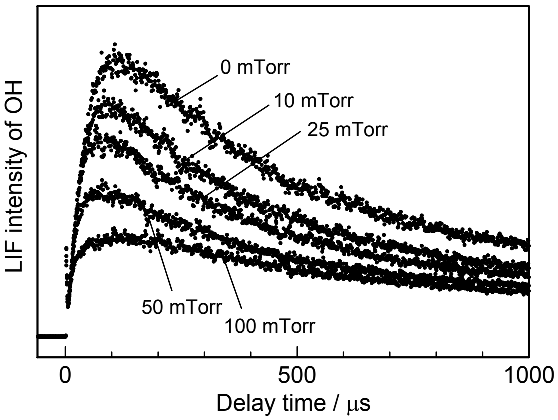


Figure 1. Time-resolved LIF intensities of $OH(X^2\Pi, v = 0)$ recorded at different pressures of CF_4. p_{NH_3} = 0.5 mTorr, p_{NO} = 5 mTorr, p_{He} = 5 Torr.

References

(1) Marcy, T. P.; Heard, D. E.; Leone, S. R. *J. Phys. Chem. A* **2002**, 106, 8249-8255.

Experimental and theoretical study of the quenching of electronically-excited oxygen with the rare gases

Shaun A Carl,[1,*] Stijn Vranckx,[2] and Duy Vu[1]

[1] Department of Chemistry, Celestijnenlaan 200F, Kaltholieke Universieit Leuven, 3001 Leuven, Belgium.
[2] Current address: Shock Wave Lab., RWTH Aachen University, Templergraben 55, 52056 Aachen, Germany
Corresponding author: Shaun.carl@chem.kuleuven.be

At moderate collision energies, collisions between electronically-excited oxygen atoms in their lowest-lying metastable O(^{1}D) state and rare gas (Rg) atoms can lead to O(^{3}P) formation via three intersections of adiabatic surfaces: the RgO($^1\Sigma^+$, $^1\Pi$) surfaces have been shown to intersect the two RgO ($^3\Sigma^-$ and $^3\Pi$) surfaces, which adiabatically correlate to O(^{3}P) + Rg(^{1}S), at three points, namely ($^1\Sigma^+/^3\Sigma^-$), ($^1\Sigma^+/^3\Pi$), and ($^1\Pi/^3\Sigma^-$).

From O(^{1}D) + Rg(^{1}S) the first two crossing points are accessed without an adiabatic barrier on the attractive RgO($^1\Sigma^{+-}$) surface, whereas the third, lying energetically above the O(^{1}D) + Rg(^{1}S) asymptote, is accessed along the repulsive ($^1\Pi$) surface and is expected to contribute a positive *T*-dependence to the overall O(^{1}D) quenching rate constant. [1]

From a theoretical perspective, Rg – O(^{1}D) provides a *relatively* simple series to study the character of molecular adiabatic states in the presence of various degrees of spin-orbit coupling due to the progression in reduced mass, and relative energy and extent of overlap of the above surface intersections. From a practical perspective, Rg-O(^{1}D) to Rg-O(^{3}P) quenching rate constants with rare gases are required for modeling oxygen-based or oxygen-seeded plasmas, and certain planetary atmospheres in order to establish the O(^{1}D) quasi-steady-state concentrations. The opposite process – triplet-to-singlet crossing – has been applied to rationalize very long distance migration (> 100 Angstrom) of O atoms in cold Xe and Kr matrices. [2]

We have performed a series of experiments to very accurately determine the magnitude and temperature dependence of rate constants, *k*, of Xe, Kr, Ar, Ne + O(^{1}D) over an extended moderate temperature range and provide and a new upper limit for the rate constant of O(^{1}D) + He below 900 K. Notably, *k* (Xe + O(^{1}D)) is the only one of the series to exhibit significant positive temperature dependence over the temperature range covered.

The rate constants determinations were carried out in a specially-designed temperature-graded reaction cell with parallel simultaneous detection of O(^{1}D) at different sections (temperatures) of the reaction chamber using a series of photomultiplier tubes. The O(^{1}D) decays were monitored in real-time using the novel chemiluminescence method employing the reaction O(^{1}D) + $C_2F_4 \rightarrow CF_2(^3B_1)$ + products.

The results are compared to our theorectical *k* predictions based on quantum statistical analysis combined with spin-orbit coupling calculations.

References

(1) Matsumi, Y.; Inagaki, Y; Morley, G. P.; Kawasaki, M. *J. Chem. Phys.* **1994** 100 , 315-324.
(2) Danilychev, A. V.; Apkarian, V. A. ; *J. Chem. Phys*. **1994** 100, 5556-5566.

Kinetics and Dynamics on the Formation of $S_2(X^3\Sigma_g^-, a^1\Delta_g)$ in the $S(^1D)$ + OCS Reaction

Jun Yamashita[1], Hirofumi Takahashi[1], Kenichi Orimi[1], Tsubasa Hashimoto[1], Hiroshi Kohguchi[1], and Katsuyoshi Yamasaki[1,*]

[1] Department of Chemistry, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8526, Japan
* Corresponding author: kyam@hiroshima-u.ac.jp

Photolysis of calbonyl sulfide (OCS) is a good source of $S(^1D)$; nevertheless, there have been few reports[1,2] on the rate coefficients of the reaction of $S(^1D)$ with OCS. The reaction of $S(^1D)$ with OCS has three exothermic channels.

$$S(^1D) + OCS \rightarrow S_2(X^3\Sigma_g^-) + CO \qquad \Delta_r H^\circ_{298} = -228\ \text{kJ mol}^{-1} \qquad (1)$$

$$\rightarrow S_2(a^1\Delta_g) + CO \qquad \Delta_r H^\circ_{298} = -172\ \text{kJ mol}^{-1} \qquad (2)$$

$$\rightarrow S(^3P) + OCS \qquad \Delta_r H^\circ_{298} = -110\ \text{kJ mol}^{-1} \qquad (3)$$

The heats of reactions of channels 1 and 2 are large enough to generate vibrationally excited $X^3\Sigma_g^-$ and $a^1\Delta_g$ states up to $v = 29$ and 22, respectively; however, van Veen et al.[1] observed the only level $v = 0$ of the $X^3\Sigma_g^-$ state, and Richter et al.[3] reported the highest populated vibrational level of the $a^1\Delta_g$ state to be $v = 6$. In this paper, the authors have determined the rate coefficient of the $S(^1D)$ + OCS reaction and detected the vibrational levels of $S_2(X^3\Sigma_g^-, a^1\Delta_g)$ higher than those reported previously.

A gaseous mixture of OCS(3–40 mTorr)/He(10 Torr) in a flow cell at 298 K was irradiated with a KrF laser (248 nm) to generate $S(^1D)$ in the photolysis of OCS. The two electronic states $X^3\Sigma_g^-$ and $a^1\Delta_g$ of S_2, produced in the $S(^1D)$ + OCS reaction, were probed with laser-induced fluorescence (LIF) via the $B^3\Sigma_u^- - X^3\Sigma_g^-$ and $f^1\Delta_u - a^1\Delta_g$ transitions, respectively. In the present measurement, vibrational levels at least $v = 15$ of $X^3\Sigma_g^-$ and $v = 10$ of $a^1\Delta_g$ were detected. Time-resolved LIF intensities of the production of the $X^3\Sigma_g^-$ state were recorded at various OCS pressures as shown in Figure 1, giving the overall rate coefficient of the $S(^1D)$ + OCS reaction to be $[3.2 \pm 0.2(2\sigma)] \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$.

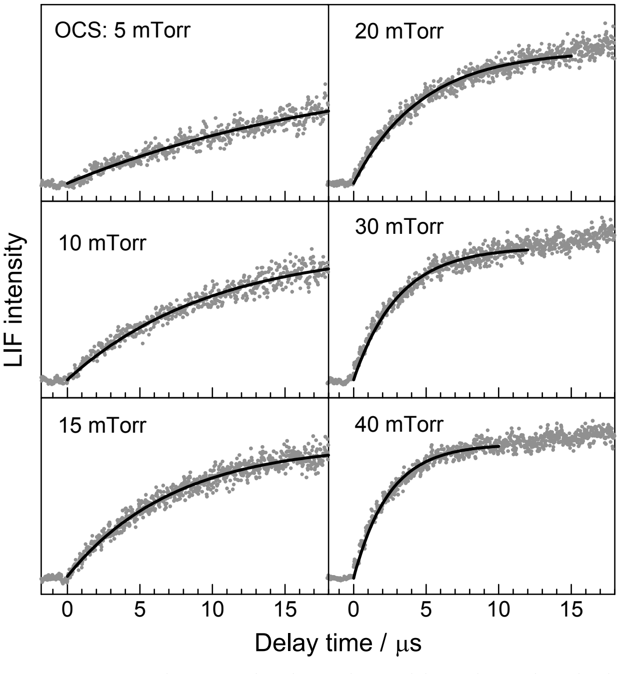


Figure 1. Time-resolved LIF intensities of 3–1 band of $S_2(B^3\Sigma_u^- - X^3\Sigma_g^-)$ transition recorded at different pressures of OCS. $p_{He} = 10$ Torr. ●: observed data and —: simulation.

References

(1) van Veen, N.; Brewer, P.; Das, P.; Bersohn, R. *J. Chem. Phys.* **1983**, 79, 4295-4301.
(2) Addison, M. C.; Byrne, C. D.; Donovan, R. J. *Chem. Phys. Lett.* **1979**, 64, 57-59.
(3) Richter, R. C.;Rosendahl, A. R.; Hynes, A. J.; Lee, E. P. F. *J. Chem. Phys.* **1998**, 109, 8876-8886.

Trends in the rate coefficients of Cl atom reactions with cyclic molecules– A comparison between cyclic ethers and hydrocarbons

H. D. Alwe, M. Walawalkar, A. Sharma, K. K. Pushpa, S. Dhanya* and P. D. Naik

Radiation & Photochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai, India 400 085.
* Corresponding author: sdhanya@barc.gov.in

The reactions of Cl atoms with VOCs contribute to the tropospheric chemistry of marine boundary layer and polluted coastal / non-coastal urban atmosphere. The reaction mechanism is very similar to that of OH radical, involving mainly abstraction of H atom, along with addition reactions in the case of unsaturated molecules. Generally, the reactivity of both OH and Cl towards unsaturated molecules is higher than that of the saturated ones, due to the higher rate coefficients of addition reactions. However, our recent measurement of rate coefficients of Cl atom reactions with unsaturated cyclic hydrocarbons at 298 K [1,2] showed an increase with number of carbon atoms (from 5-8), but no significant change with unsaturation. To further understand these trends as compared to that of OH radical reactions, rate coefficients of reaction of Cl atom with cyclic ethers, including one with unsaturation, are measured at 298 K using relative rate method.

The molecules studied are tetrahydropyran (THP), tetrahydrofuran (THF) and 2,5-dihydrofuran (DHF). These cyclic ethers are known to react very fast with OH radicals, their reactivity being higher than that of the corresponding hydrocarbons. The recent relative rate measurements of the rate coefficients of reactions of Cl atoms with THP and THF show the reactivity of THP to be lower than that of THF in spite of increased number of CH_2 groups, and no clear trend is observed in the reactivity of Cl atoms with the corresponding hydrocarbons [3].

The present measurements on THP and THF are carried out with reference to n-pentane, n-hexane and 1-butene, which are different from the reference molecules used in the previous reports. The relative ratios are not affected by the presence of oxygen. The average values of the rate coefficients are (2.52 ± 0.36), (2.52 ± 0.38) and $(4.48 \pm 0.59) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} for THP, THF and DHF, respectively. The rate coefficients for THP and THF agree well with the earlier reports and confirm that there is no increase in the rate coefficient of THP as compared to that of THF. It is also observed that unlike cyclic hydrocarbons, there is an increase in the rate coefficients with unsaturation in the ring. While the logarithmic values of the rate coefficients of OH reactions with cyclic hydrocarbons and ethers together correlate very well with HOMO energy, it is not found to be satisfactory in the case of rate coefficients of Cl atom reactions. The rate coefficients of Cl atom reactions, approaching collision controlled limits, do not correlate well with molecular size either when both hydrocarbons and ethers are considered together.

References

1. Sharma, A.; Pushpa, K. K.; Dhanya, S.; Naik, P. D.; Bajaj, P. N. *Int. J. Chem. Kinet.* **2010**, 42, 98 – 105.
2. Sharma, A.; Pushpa, K. K., Dhanya, S., Naik, P. D., Bajaj, P. N. *Int. J. Chem. Kinet.* **2011**, 43, 431 – 440.
3. Giri, B. R.; Roscoe, J. M. *J. Phys. Chem. A* **2010**, 114, 8369 – 8375.

Ozonolysis of a series of branched alkenes: Kinetics and gas-phase products

M. Duncianu,[1,2] V. Riffault,[1,2,*] R.I. Olariu,[3] C. Arsene,[3] T. Braure,[1,2] A. Tomas,[1,2] P. Coddeville,[1,2] and Y. Bedjanian[4]

[1] Université Lille Nord de France, F-59000, Lille, France
[2] EMDouai, CE, F-59508, Douai, France
[3] "Al. I. Cuza" University of Iasi, Faculty of Chemistry, 11 Carol I, 700506, Iasi, Romania
[4] Institut de Combustion, Aérothermique, Réactivité et Environnement (ICARE), CNRS, F-45071, Orléans, France
* Corresponding author: veronique.riffault@mines-douai.fr

The ozonolysis reactions of a series of branched alkenes have been investigated at room temperature and atmospheric pressure using a laminar flow reactor newly developed in our laboratory (1). This device allows the monitoring of the first steps of ozonolysis reactions (typically ~30 s to 5 minutes) providing complementary data to more widely performed smog chamber experiments.

Rate coefficients have been measured under pseudo first-order conditions in excess of the alkene. The decay of ozone has been monitored with an O_3 analyzer while alkene concentrations have been determined using online sampling onto adsorbent cartridges followed by thermodesorption and subsequent analysis in a GC/FID-MS system. Additional experiments carried out in a smog chamber showed good agreement with the flow reactor data and literature values.

Products from the ozonolysis of 2,4,4-trimethyl-2-pentene has been specifically studied. The experimental results are supportive of the general Criegee mechanism for alkene ozonolysis, in agreement with the literature (e.g. (2)) and the formation of a non-oxidized alkene has been identified and quantified (Figure 1).

Our laboratory participates in the Research Institute of Industrial Environment (IRENI) which is financed by the Communauté Urbaine de Dunkerque, the Nord-Pas de Calais Regional Council, the French Ministry of Education and Research, and European funds (FEDER). R.I. Olariu and C. Arsene acknowledge the EMDouai and the IRENI for Invited Professor Fellowships. M. Duncianu is grateful for a PhD scholarship from the Nord-Pas de Calais Regional Council and Armines. T. Braure is funded by a PhD grant from Armines.

References

(1) Duncianu, M.; Olariu, R.I.; Riffault, V.; Visez, N.; Tomas, A.; Coddeville, P. *J. Phys. Chem. A* **2012**, Article ASAP; DOI 10.1021/jp211480x.
(2) Grosjean, E.; Grosjean, D. *Environ. Sci. Technol.* **1997**, *31*, 2421-2427.

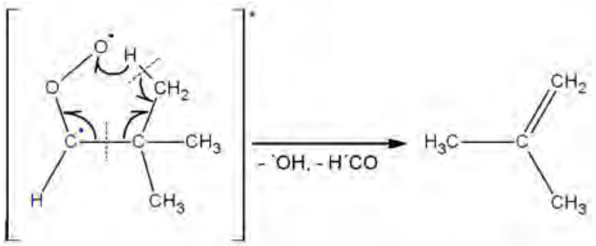


Figure 1. Suggested mechanism for the formation of 2-methyl-2-propene via one of the Criegee intermediates formed in the ozonolysis of 2,4,4-trimethyl-2-pentene

New Mechanistic Insights to the O(^{3}P) + Propene Reaction from Multiplexed Photoionization Mass Spectrometry

John D. Savee,[1] Oliver Welz,[1] Craig A. Taatjes,[1] and David L. Osborn[1,*]

[1] Combustion Research Facility, Sandia National Labs, Livermore, CA, USA
* Corresponding author: dlosbor@sandia.gov

The reaction of O(^{3}P) with unsaturated hydrocarbons is a critical part of the rich oxidation chemistry that occurs in combustion. At low temperatures, the general mechanism for these types of reactions begins with electrophilic attack of O(^{3}P) on a carbon atom from the unsaturated carbon-carbon bond to form a triplet biradical species that can then isomerize, dissociate, or undergo collisional stabilization.[1] In the case of O(^{3}P) + acetylene (C_2H_2), observed products can be explained entirely by reaction on the initial triplet potential energy surface (PES).[2,3] However, in the case of O(^{3}P) + ethene (C_2H_4), recent experiments and calculations suggest that intersystem crossing (ISC) to the singlet PES is surprisingly facile.[4,5] The role of ISC in larger alkenes is difficult to ascertain using existing theoretical approaches, thus making experimental measurements critical to our general understanding of these reactions.

The case of O(^{3}P) + propene (C_3H_6) and the rich chemistry available to this prototypical larger alkene has received little attention. In the present experiments, multiplexed photoionization mass spectrometry is applied to the reaction of O(^{3}P) + C_3H_6 to provide a global 'image' of this fundamental chemical reaction.[6,7] Coupled with tunable vacuum ultraviolet radiation from the Advanced Light Source synchrotron, this time-resolved account of all photoionizable products allows quantitative isomer-resolved identification of primary and secondary products. In light of the few theoretical characterizations of relevant C_3H_6O PESs[8,9] our results indicate that, like the case of O(^{3}P) + C_2H_4, significant ISC must be invoked to explain the observed products. These results offer considerable mechanistic insight that can be used in future theoretical accounts of the O(^{3}P) + C_3H_6 reaction.

References

(1) Cvetanovic, R. J.; Singleton, D. L. *Rev. Chem. Int.* **1984**, 5, 183.
(2) Capozza, G.; Segoloni, E.; Leonori, F.; Volpi, G. G.; Casavecchia, P. *J. Chem. Phys.* **2004**, 120, 4557.
(3) Nguyen, T. L.; Vereecken, L.; Peeters, J. *J. Phys. Chem. A* **2006**, 110, 6696.
(4) Casavecchia, P.; Capozza, G.; Segoloni, E.; Leonori, F.; Balucani, N.; Volpi, G. G. *J. Phys. Chem. A* **2005**, 109, 3527.
(5) Nguyen, T. L.; Vereecken, L.; Hou, X. J.; Nguyen, M. T.; Peeters, J. *J. Phys. Chem. A* **2005**, 109, 7489.
(6) Osborn, D. L.; Zou, P.; Johnsen, H.; Hayden, C. C.; Taatjes, C. A.; Knyazev, V. D.; North, S. W.; Peterka, D. S.; Ahmed, M.; Leone, S. R. *Rev. Sci. Instrum.* **2008**, 79, 104103.
(7) Taatjes, C. A.; Hansen, N.; Osborn, D. L.; Kohse-Hoinghaus, K.; Cool, T. A.; Westmoreland, P. R. *Phys. Chem. Chem. Phys.* **2008**, 10, 20.
(8) Zhang, W.; Du, B.; Feng, C. *J. Mol. Struct.* **2007**, 806, 121.
(9) DeBoer, G. D.; Dodd, J. A. *J. Phys. Chem. A* **2007**, 111, 12977.

Oxalyl Chloride, $(COCl)_2$, UV Spectrum and Cl Quantum Yields at 193, 248 and 351 nm, and the Kinetics of the ClCO + M Reaction

Buddhadeb Ghosh,[1,2,*,†] Dimitrios K. Papanastasiou,[1,2] and James B. Burkholder[1]

[1] Earth System Research Laboratory, Chemical Sciences Division, NOAA, Boulder CO 80305.
[2] Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder CO 80309.
[†] Current address: Water and Air Group, Sustainability Technologies, Research & Development, ConocoPhillips. Bartlesville, OK 74004
* Corresponding author: Bud.Ghosh@conocophillips.com

Oxalyl chloride, $(COCl)_2$, is commonly used in laboratory studies as a photolytic precursor of Cl atoms. Here, we report the UV-Vis absorption spectrum of $(COCl)_2$ between 200 and 450 nm at 298 K measured using diode array spectroscopy and the Cl quantum yield, $\Phi(\lambda)$, in the pulsed laser photolysis of $(COCl)_2$ at 193, 248, and 351 nm measured at 298 K using atomic resonance fluorescence. Oxalyl chloride UV photolysis occurs via an impulsive three-body dissociation mechanism into CO, Cl, and ClCO*

$$(COCl)_2 + h\nu \rightarrow ClCO^* + Cl + CO \qquad (1)$$

where excited ClCO, ClCO*, can subsequently dissociate or stabilize

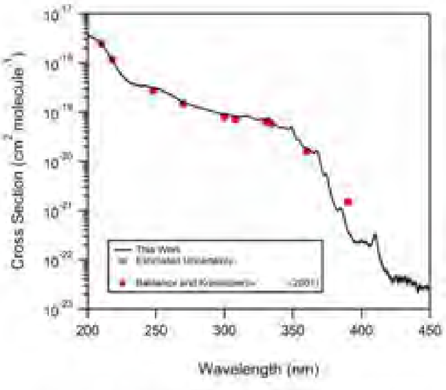
$$ClCO^* \rightarrow Cl + CO \qquad (2a)$$

$$\rightarrow ClCO \qquad (2b)$$

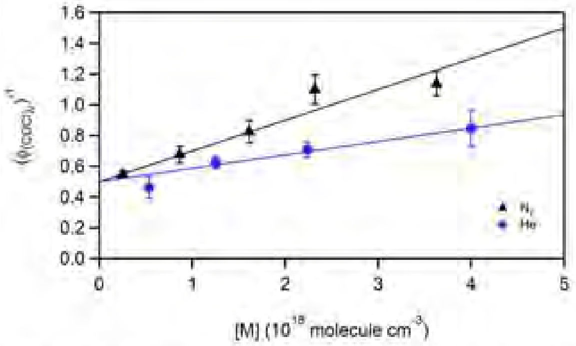
ClCO is thermally unstable under the temperatures and pressures of our experiments

$$ClCO + M \rightarrow Cl + CO + M \qquad (3)$$

leading to the formation of a Cl atom, which was resolvable in the Cl atom temporal profile. At 193 nm, $\Phi(\lambda)$ was found to be 2.07 ± 0.37 and consistent with a branching ratio for channel 2a greater than 0.9. At 248 nm, a branching ratio of 0.80 for channel 2a was determined, while the overall Cl atom quantum yield, following the completion of reaction 3, was found to be 1.98 ± 0.26, independent of bath gas pressure (15-70 Torr). The photolysis quantum yield at 351 nm was pressure dependent suggesting the involvement of a long-lived excited electronic state. In the low-pressure limit the overall Cl atom quantum yield was 2 ± 0.22. The $\Phi(\lambda)$ measurements and interpretation will be discussed. The thermal decomposition rate coefficient of ClCO was measured as part of this work over the 13-128 Torr pressure range at temperatures between 253 and 298 K with He and N_2 bath gas. Our results will be compared with results from previous studies.



UV-Vis spectrum of oxalyl chloride.



Stern-Volmer plot for the 351 nm photolysis of oxalyl chloride.

Determination of the Rate Constants for the $NH_2(X^2B_1)$ + $NH_2(X^2B_1)$ and $NH_2(X^2B_1)$ + H Recombination Reactions with Collision Partners CH_4, C_2H_6, CO_2, CF_4, and SF_6 at Low Pressures and 296 K

Gokhan Altinay and R. Glen Macdonald*

Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439-4381

The recombination rate constants for the reactions $NH_2(X^2B_1) + NH_2(X^2B_1) + M$ and $NH_2(X^2B_1) + H + M$, where M was CH_4, C_2H_6, CO_2, CF_4, or SF_6, were measured in the same experiment over the pressure range 1 to 20 Torr and 7 to 20 Torr, respectively, at 296±2 K. The NH_2 radical was produced by the 193 nm laser photolysis of NH_3. Both NH_2 and NH_3 were monitored simultaneously following the photolysis laser pulse. High-resolution time-resolved absorption spectroscopy was used to monitor the temporal dependence of both species: NH_2 on the $^{1}2_{21} \leftarrow {}^{1}3_{31}$ rotational transition of the $(0,7,0)A^2A_1 \leftarrow (0,0,0)X^2B_1$ electronic transition near 675 nm and NH_3 in the IR on either of the inversion doublets of the $^{q}Q_3(3)$ rotational transition of the ν_1 fundamental near 2999 nm. The NH_2 self-recombination clearly exhibited fall-off behavior for the third-body collision partners used in this work. The pressure dependences of the NH_2 self-recombination rate constants were fit using Troe's parameterization scheme, k_{inf}, k_0, and F_{cent}, with $k_{inf} = 7.9 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, the theoretical value calculated by Klippenstein et al.(1) The individual Troe parameters were: CH_4,$k_0^{CH_4} = 9.4 \times 10^{-29}$ and $F_{cent}^{CH_4} = 0.61$; C_2H_6, $k_0^{C_2H_6} = 1.5 \times 10^{-28}$ and $F_{cent}^{C_2H_6} = 0.80$; CO_2, = $k_0^{CO_2}$ 8.6×10^{-29} and $F_{cent}^{CO_2} = 0.66$; CF_4, $k_0^{CF_4} = 1.1 \times 10^{-28}$ and $F_{cent}^{CF_4} = 0.55$; SF_6, $k_0^{SF_6} = 1.9 \times 10^{-28}$ and $F_{cent}^{SF_6} = 0.52$, where the units of k_0 are cm^6 $moleule^{-2}$ s^{-1}. The $NH_2 + H + M$ reaction rate constant was assumed to be in the three-body pressure regime, and the association rate constants were: CH_4, $(6.0 \times 10^{-30}$; C_2H_6, $(1.1 \times 10^{-29}$; CO_2, $(6.5 \pm 1.8) \times 10^{-30}$; CF_4, $(8.3 \pm 1.7) \times 10^{-30}$; SF_6, $(1.4 \pm 0.30) \times 10^{-29}$, with units cm^6 $molecule^{-1}$ s^{-1}, and the systematic and experimental errors are given at the 2σ confidence level

References

(1) J. Phys. Chem A. **113**, *113,* 10241

Differences in OH Reactivity Between the (*E*)- and (*Z*)- Isomers of $CF_3CH=CHCF_3$

Munkhbayar Baasandorj,[1,2] A.R. Ravishankara,[1] and James B. Burkholder[1]*

[1] Earth System Research Laboratory, Chemical Sciences Division, National Oceanic and Atmospheric Administration, 325 Broadway, Boulder, CO, USA
[2] Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO, USA
* Corresponding author: James.B.Burkholder@noaa.gov

Unsaturated hydrofluorocarbons (hydrofluoroolefins, HFO) are currently being considered as potential replacements for hydrochlorofluorocarbons (HCFCs) and saturated-hydrofluorocarbons (HFCs) in various commercial applications. (*E*)- and (*Z*)- $CF_3CH=CHCF_3$ are replacement candidates but before used commercially their atmospheric fate and potential impacts on the environment need to be fully assessed. A significant atmospheric loss process for these compounds is expected to be their gas-phase reaction with the OH radical.

A study of the OH reaction kinetics of (*Z*)-$CF_3CH=CHCF_3$ was recently reported from our laboratory.[1] The reaction rate coefficient, *k*, has a non-Arrhenius behavior with a negative temperature dependence at temperatures <300 K. The rate coefficient for the OH + (*E*)-$CF_3CH=CHCF_3$ reaction was measured in this study using pulsed laser photolysis–laser induced fluorescence (PLP–LIF) and relative rate techniques. Rate coefficients were measured over a range of temperature (212 – 373) K and total pressure (20 – 600 Torr; He, N_2). The rate coefficient was found to be independent of pressure and showed Arrhenius behavior over the temperature range of the measurements. The profound differences in the reactivity of the (*E*)- and (*Z*)- isomers are discussed.

References

(1) Baasandorj, M; A.R. Ravishankara, and J. B. Burkholder, J. Phys. Chem. A 2012, 115, 10539-10549.

Chemical Reaction Rates from Ring Polymer Molecular Dynamics

Yu. V. Suleimanov,[1,2*] J. W. Allen,[1] and W. H. Green[1]

[1] Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

[2] Department of Mechanical and Aerospace Engineering, Combustion Energy Frontier Research Center, Princeton University, Princeton, New Jersey 08544
* Corresponding author: ysuleyma@mit.edu

There is considerable current interest in the inclusion of quantum mechanical (zero point energy and tunneling) effects in the calculation of chemical reaction rates. The importance of these effects is well known: changes in zero point energy between the reactants and the transition state are responsible for the observed kinetic isotope effects in a wide variety of reactions, and tunneling can increase the rate of an activated proton transfer reaction at low temperatures by several orders of magnitude. The exact inclusion of these effects in calculations of chemical reaction rates is still however a very challenging task, because the computational effort that is needed to solve the reactive scattering Schrödinger equation increases exponentially with the number of atoms in the reaction.

A number of approximate methods have been proposed to overcome this problem and to provide a practical way to include these effects in reaction rate calculations. One of the most promising of these is recently developed ring polymer molecular dynamics (RPMD) model [1-3]. This model is based on imaginary time Feynman path integration and exploits the isomorphism between the quantum statistical mechanics of a single particle and the classical statistical mechanics of a fictitious ring polymer. It leads to a reaction rate theory that is essentially a classical rate theory in an extended (*n*-bead imaginary time path integral) phase space, and it is therefore directly applicable to complex chemical reactions in their full dimensionality.

In this work, we develop an efficient computational procedure for calculating the rates of bimolecular chemical reactions in the gas phase within the RPMD approximation. A key feature of the procedure is that it does not require that one calculate the absolute quantum mechanical partition function of the reactants or the transition state: The rate coefficient only depends on the ratio of these two partition functions which can be obtained from a thermodynamic integration along a suitable reaction coordinate. The procedure is illustrated with applications to several three-dimensional three-atomic reactions and the six-atomic $H+CH_4$ reaction, for which well-converged quantum reactive scattering results are available for comparison, as well as to several more complex reactions, for which exact reactive scattering calculations are impossible. The ring polymer rate coefficients agree with the exact results at high temperatures and are within a factor of 2-3 of the exact results at temperatures in the deep quantum tunneling regime, where the classical rate coefficients are too small by several orders of magnitude. This is certainly good enough to encourage future applications of RPMD to complex chemical reactions.

References

(1) Suleimanov, Yu. V; Collepardo-Guevara, R.; Manolopoulos, D. E. *J. Chem. Phys.* **2011**, 134, 044131.
(2) Perez de Tudela, R.; Aoiz, F. J.; Suleimanov, Yu. V.; Manolopoulos, D. E. *J. Phys. Chem. Lett.* **2012**, 3 493.
(3) Collepardo-Guevara, R.; Suleimanov, Yu. V.; Manolopoulos, D. E. *J. Chem. Phys.* 2009, 130, 174713.

Low temperature formation of cyanopolyynes

Sidaty Cheikh Sid Ely[1], Stephen J. Klippenstein,[2] Jean-Claude Guillemin[3] and Ian R. Sims[1,*]

[1] Institut de Physique de Rennes, UMR CNRS-UR1 6251, Université de Rennes 1, 263 Avenue du Général Leclerc, 35042 Rennes Cedex, France
[2] Chemistry Division, Argonne National Laboratory, Argonne, IL 60439, U.S.A.
[3] Ecole Nationale Supérieure de Chimie de Rennes, CNRS UMR 6226, Avenue du Général Leclerc, CS 50837, 35708 Rennes Cedex 7, France
* Corresponding author: ian.sims@univ-rennes1.fr

It is thought that long chain cyanopolyyne molecules $H(C_2)_nCN$ may play an important role in the formation of the orange haze layer in Titan's atmosphere. The longest carbon chain molecule observed in interstellar space, $HC_{11}N$, is also a member of this series. We have proposed (1) a low temperature gas-phase synthetic route to produce these species involving successive radical molecule reactions as follows:

$$C_2H + H(C{\equiv}C)_nH \rightarrow H(C{\equiv}C)_{n+1}H + H \quad (1) \qquad CN + H(C{\equiv}C)_nH \rightarrow H(C{\equiv}C)_nCN + H \quad (2)$$

$$C_2H + H(C{\equiv}C)_nCN \rightarrow H(C{\equiv}C)_{n+1}CN + H \quad (3) \qquad CN + H(C{\equiv}C)_nCN \rightarrow NC(C{\equiv}C)_nCN + H \quad (4)$$

The first three reaction categories lead to growth of (cyano)polyynes. However, the fourth category of reaction could act as a 'termination reaction' for this chain as the dicyanopolyyne is likely to be relatively unreactive. Reactions of type (1) and (2) have been shown by us to be rapid down to ~20 K for the first member of the series, acetylene ($n = 1$) (1,2), but no further studies have been made owing to the fact that the necessary molecular reagents have to be synthesised.

Using a combination of the CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme, or Reaction Kinetics in Uniform Supersonic Flow) technique coupled with pulsed laser photochemical kinetics methods (3,4) as well as a number of technical developments including a new pulsed CRESU (5), reaction types (1) and (2) have been studied for the next member of the series, diacetylene, H-C≡C-C≡C-H, and reaction types (3) and, crucially, (4) have been studied with the first member of the series, cyanoacetylene, H-C≡C-C≡N (6,7).

The experimental results will be compared to new variable reaction coordinate transition state theory (VRC-TST) calculations of the addition kinetics. The calculations also provide some indication of the expected addition sites and likely products. Master equation simulations are used to predict the pressure dependence of the kinetics, including the rate of radiative stabilization at low pressure. Additional calculations predict that the reactions of CN / CCH with NC_4N will be slow in Titan's atmosphere due to the presence of significantly positive barriers.

References

(1) Chastaing, D.; James, P. L.; Sims, I. R.; Smith, I. W. M. *Faraday Discuss.* **1998**, 109, 165-181.
(2) Sims, I. R.et al. *Chem. Phys. Lett.* **1993**, 211, 461-468.
(3) Sims, I. R.et al. *J. Chem. Phys.* **1994**, 100, 4229-4241.
(4) James, P. L.et al. *J. Chem. Phys.* **1998**, 109, 3882-3897.
(5) Morales, S. B. PhD, Université de Rennes 1, 2009.
(6) Cheikh Sid Ely, S.; Morales, S. B.; Guillemin, J.-C.; Sims, I. R. **2012**, in preparation.
(7) Halpern, J. B.; Miller, G. E.; Okabe, H. *Chem. Phys. Lett.* **1989**, 155, 347-350.

Atmospheric reactivity of functionalized organic nitrates

R. Suarez-Bertoa*, B. Picquet-Varrault, W. Tamas, E. Pangui, C. Gaimoz, R. Durand-Jolibois, J-F. Doussin

Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA) Universities of Paris Est-Créteil and Diderot, Créteil, France
* Corresponding author: ricardo.suarez@lisa.u-pec.fr

Organic nitrates are important species of the tropospheric reactive nitrogen budget. They are mainly formed in NOx rich air by the degradation of hydrocarbons initiated by OH (daytime) and NO_3 (nighttime) radicals. Organic nitrates lifetimes are in the order of several days or weeks (1, 2). Thus, they may behave as reservoirs for reactive nitrogen by undergoing long-range transport in the free troposphere before decomposing to release NOx in remote regions. They, therefore, play a key role in the distribution of the reactive nitrogen and consequently in the ozone formation and distribution in remote areas. Among these organic nitrates, polyfunctional species such as α,β-hydroxynitrates and ketonitrates can be formed(3).
Several experimental works have been performed on the alkyl nitrates reactivity with OH radicals and their photolysis (1,2,4) but very few studies have been carried out on functionalized organic nitrates (hydroxynitrates, dinitrates, ketonitrates, etc)(5, 6). These last compounds have yet been shown to contribute significantly to the NOy budget in rural and urban areas (7). Moreover, recent modelling studies have pointed out that the ozone budget in rural area is very sensitive to the fate of functionalized isoprene nitrates (8, 9).
Thus, a study aimed at obtaining a better knowledge and understanding of the functionalized organic nitrates reactivity in the atmosphere is in progress and the first kinetic results on the reactivity and photolysis rates of a series of ketonitrates will be presented here.

References

(1) Becker, K.H. and Wirtz, K. *J. Atmos. Chem.* **1989**, 9, 419-433.
(2) Clemitshaw, K.C.; Williams, J.; Rattigan, O.V.; Shallcross, D.E.; Law, K.S. and Cox, R.A. *J. Photoch. Photobio. a*. **1997**, 102, 117-126.
(3) Muthuramu, K.; Shepson, P. B.; Obrien, J. M. *Environ. Sci. Technol.* **1993**, 27, 1117-1124.
(4) Talukdar, R.K.; Herndon, S.C.; Burkholder, J.B.; Roberts, J.M. and Ravishankara, A.R. *J. Chem. Soc. Faraday T.* **1997**, 93, 2787-2796.
(5) Barnes, I., Becker, K.H. and Zhu, T. *J. Atmos. Chem.* **1993**, 17, 353-373.
(6) Treves, K. and Rudich, Y. *J. Phys. Chem. A.* **2003**, 107, 7809-7817.
(7) Kastler J.; Jarman W.; Ballschmiter K. *Fresenius J. Anal. Chem.* **2000**, 368, 244-249.
(8) Horowitz, L.W.; Fiore, A.M.; Milly, G.P.; Cohen, R.C.; Perring, A.; Wooldridge, P.J. *et al.* *J. Geophys. Res*. **2007**, 112, D12S08.
(9) Curci, G.; Beekmann, M.; Vautard, R.; Smiatek, G.; Steinbrecher, R.; Theloke, J. *et al.* *Atmos. Environ.* **2009**, 43, 1444-1455.

Pressure and temperature dependence of methyl nitrate formation in the CH_3O_2 + NO reaction

Nadezhda Butkovskaya[1], Alexandre Kukui[2] and Georges Le Bras[1,*]

[1] Institut de Combustion, Aérothermique, Réactivité et Environnement (ICARE), CNRS, Orléans, France
[2] Laboratoire Atmosphères, Milieux, Observations Spatiales (LATMOS), CNRS-IPSL, Guyancourt, France
[*] Corresponding author : georges.lebras@cnrs-orleans.fr

Reactions of alkyl peroxy radicals, RO_2, with NO are recognized to potentially reduce tropospheric ozone formation through their minor channel producing organic nitrates, acting as both RO_x and NO_x reservoir or sink species. The nitrate yields previously measured for these reactions range from a few percents for small alkyl nitrates ($C \geq 2$) to ≈ 30% for long-chain alkyl nitrates ($C \geq 7$), at room temperature and atmospheric pressure. For the methyl nitrate yield in the reaction:

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \qquad (1a)$$
$$\rightarrow CH_3ONO_2 \qquad (1b)$$

only an upper limit of 3% has been determined so far at 295 K and 100 Torr (1). However, even at a lower CH_3ONO_2 yield, channel (b) may still be of tropospheric significance considering both the importance of the CH_3O_2 radical as intermediate in the oxidation of methane and other major VOCs, and the long lifetime of CH_3ONO_2 (one week to one month).

The study of methyl nitrate formation in reaction (1) has been carried out using a turbulent flow reactor coupled with a chemical ionisation mass spectrometer (TFR-CIMS). This set up has been previously used to investigate the formation of ethyl nitrate and isopropyl nitrate in reactions of NO with ethyl peroxy and isopropyl peroxy radicals, respectively (2, 3). The branching ratio $\beta = k_{1b}/k_{1a}$ has been determined over the pressure and temperature ranges 50-500 Torr and 220-300 K, respectively. Methyl nitrate was generated in the TFR from $F/CH_4/O_2/NO$ mixtures where CH_3O produced reacted predominantly with NO. β was determined from the CH_3ONO_2/CH_2O and CH_3ONO_2/CH_3ONO product concentration ratios where CH_2O and CH_3ONO were produced in the two channels of the CH_3O + NO reaction. These three products were calibrated by generating them *in situ* from $F/CH_3OH/NO_2$ and $F/CH_3OH/NO$ mixtures. All the species were detected by PTR from H_3O^+ and its water clusters, except NO_2 detected by electron transfer from SF_6^-. At 298 K, the branching ratio β has been found to increase linearly with pressure from (0.33 ± 0.16)% at 50 Torr to (0.80 ± 0.54)% at 500 Torr. Decrease of temperature from 300 K to 220 K leads to an increase of β by a factor of about 3 in the 100-200 Torr range. These data correspond to a value of $\beta \approx (1.0 \pm 0.7)\%$ over the pressure and temperature ranges of the whole troposphere.
The atmospheric concentrations of methyl nitrate estimated using these results have been compared to those measured in different atmospheric environments.

References

(1) Scholtens, K.W. ; Messer, B.M. ; Cappa, C.D. ; Elrod, M. *J. Phys. Chem. A*, **1999**, 103, 4378-4384.
(2) Butkovskaya, N.; Kukui, A.; Le Bras, G. *J. Phys. Chem. A* **2010**, 114, 956-964.
(3) Butkovskaya, N.; Kukui, A.; Le Bras, G. *Z. Phys. Chem.* **2010**, 224, 1025-1038.

Photochemistry of organic nitrates studied using cavity ring-down spectroscopy

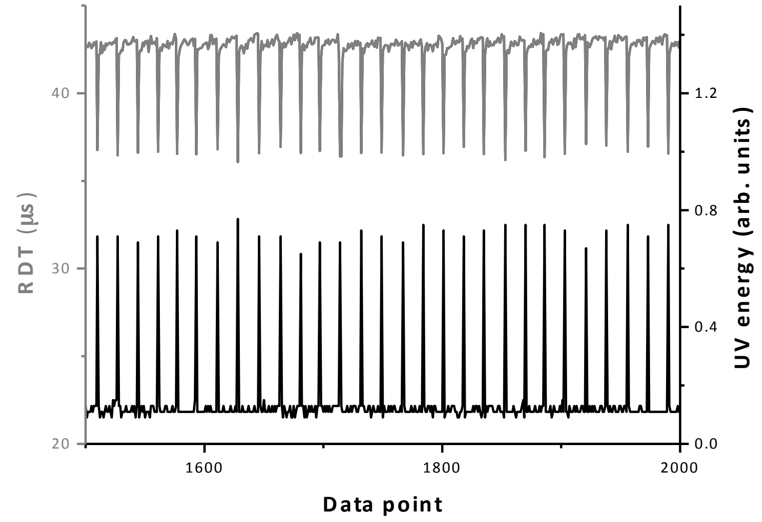
Christina M. Higgins[1], and Andrew J. Orr-Ewing[1*]

[1] School of Chemistry, University of Bristol, United Kingdom
* Corresponding author: A.Orr-Ewing@bristol.ac.uk

Organic nitrates ($RONO_2$) are important trace species in atmospheric chemistry. They have the potential to act as temporary NO_x reservoirs, allowing for transportation of NO_x over large distances and affecting regional air chemistry.

$RONO_2$ compounds exhibit broad, unstructured UV absorption spectra that steeply decrease in cross section with increasing wavelength. The absorption spectra show an intense band at 190 – 220 nm, resulting from $\pi - \pi^*$ transitions. A weaker band, assigned to $n - \pi^*$ excitation extends to approximately 330 nm. It is this latter absorption that is responsible for tropospheric photolysis of $RONO_2$.

Absorption cross sections, NO_2 quantum yields and photolysis lifetimes have been measured for various $RONO_2$ compounds at tropospherically relevant ultraviolet wavelengths from 295 – 320 nm. Cavity ring-down spectroscopy has been used to detect NO_2 produced during $RONO_2$ photolysis. For isopropyl nitrate ($C_3H_7ONO_2$), at photolysis wavelengths of 295 and 315 nm, the NO_2 quantum yield has been found to be unity.



Typical experimental data for isopropyl nitrate (3.6 Torr partial pressure) at a photolysis wavelength of 295 nm (0.7 mJ/pulse).

Halothane, Isoflurane, Enflurane, Desflurane, and Sevoflurane: Atmospheric Chemistry and Environmental Impact of General Anesthetic Gases

Mads P. Sulbaek Andersen[1,*], B. Karpichev[1], Timothy J. Wallington[2], Ole J. Nielsen[3], S. P Sander[1]

[1] Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, USA
[2] Systems Analytics and Environmental Sciences Department, Ford Motor Company, Dearborn, MI, USA
[3] Department of Chemistry, University of Copenhagen, Copenhagen, Denmark
* Corresponding author: mads@sulbaek.dk

The atmospheric chemistry of halothane ($CF_3CHClBr$), isoflurane ($CF_3CHClOCHF_2$), enflurane ($CHFClCF_2OCHF_2$), desflurane ($CF_3CHFOCHF_2$) and sevoflurane ($(CF_3)_2CHOCH_2F$) has been investigated using laser photolysis/laser induced fluorescence and FTIR/smog chamber techniques. The kinetics of reactions with OH radicals and Cl atoms have been measured and the products resulting from the OH radicals and chlorine atom initiated oxidation have been identified. For the first time, measured absorption cross sections of the anesthetics were weighted by an instantaneous cloudy-sky radiative forcing calculated for a model atmosphere, allowing for a more accurate evaluation of the global warming potentials for this selection of important medical compounds. The results will be discussed with respect to the impact of inhaled anesthetics on the radiative forcing of climate change.

trans-$CF_3CH=CHCl$: Temperature Dependent OH Rate Coefficients and Global Warming Potential

Tomasz Gierczak,[1,2,3] M. Baasandorj,[1,2] and James B. Burkholder[3,*]

[1] Earth System Research Laboratory, Chemical Sciences Division, National Oceanic and Atmospheric Administration, 325 Broadway, Boulder Colorado, 80305, USA.
[2] Cooperative Institute for Research in Environmental Sciences, U. of Colorado, Boulder Colorado, 80309, USA.
[3] Permanent address: Dept. of Chemistry, Warsaw University, al. Żwirki i Wigury 101, 02-089 Warszawa, Poland
* Corresponding author: James.B.Burkholder@noaa.gov

trans-$CF_3CH=CHCl$ is a proposed replacement compound for chlorofluorocarbons (CFCs) and hydrofluorocarbons (HFCs) with a possible industrial use as a foam blowing agent. For replacement compounds to be environmentally acceptable, their ozone depletion potentials (ODPs) and global warming potentials (GWPs) need to be negligible. In order to quantify ODPs and GWPs the atmospheric lifetimes and infrared absorption cross sections of the replacement compound are required. The primary atmospheric loss process for *trans*-$CF_3CH=CHCl$ is expected to be its gas-phase reaction of hydroxyl radical, OH

$$OH + trans\text{-}CF_3CH=CHCl \rightarrow \text{products} \qquad (1)$$

Reaction (1) is expected to proceed predominately via addition of the OH radical to the carbon-carbon double bond at both the central and terminal carbon sites. In this work, rate coefficients, $k_1(T)$, for reaction (1) were measured between 213 and 376 K at 25–100 Torr (He/N_2). Rate coefficients were measured under pseudo-first-order conditions in OH with OH produced by the 248 nm pulsed laser photolysis of H_2O_2, HNO_3, or $(CH_3)_3COOH$. OH loss was monitored using laser-induced fluorescence. $k_1(T)$ was found to be independent of pressure over this range with $k_1(296\text{ K}) = (3.76 \pm 0.35) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}. The quoted uncertainties in $k_1(T)$ are at the 2σ (95% confidence) level and include estimated systematic errors. The atmospheric lifetime of *trans*-$CF_3CH=CHCl$ was determined to be ~34 days, although the actual atmospheric lifetime for such a short-lived molecule will depend on the location and season of its emission. The infrared absorption spectrum of *trans*-$CF_3CH=CHCl$ was measured in this work and the GWP of *trans*-$CF_3CH=CHCl$ calculated. The present results will be compared with results from a previous room temperature study[1] and the reactivity of other halogenated propenes. The atmospheric implications of this work will also be discussed.

References

(1) Sulbaek Andersen, M.P.; Nilsson, E.J.K.; Nielsen, O.J., Johnson, M.S., Hurley, M.D., Wallington, T.J. *J. Photochem. and Photobio. A, Chem.* **2008**, 199, 92-97.

Environmental Characteristics of Next Generation Commercial Hydrofluorocarbons: HFO-1234yf and HFO-1336mzz

Robert Waterland ,[1*] Mark Russell,[2] Gerco Hoogeweg,[3] and Robert Hoke[2]

[1] Central Research & Development, E. I. du Pont de Nemours & Co. Inc, Wilmington, DE, USA
[2] Haskell Global Centers for Health and Environmental Sciences, E. I. du Pont de Nemours & Co., Inc, Newark, DE, USA
[3] Waterborne Environmental, Inc., Leesburg, VA, USA
* Corresponding author: Robert.L.Waterland@usa.dupont.com

HFO-1234yf ($CF_3CF=CH_2$) and HFO-1336mzz ($CF_3CH=CHCF_3$) are being commercialized as replacements for the current generation of hydrofluorocarbon and hydrocarbon refrigerants and foam expansion agents. These unsaturated compounds are short-lived in the atmosphere and have modest environmental footprints. We will discuss the environmental characteristics of the title compounds and their principal atmospheric degradation products.

References

(1) Luecken, D.J.; Waterland, R.L.; Papasavva, S.; Taddonio, K.N.; Hutzell, W.T.; Rugh, J.P.; Andersen, S.O. *Environ. Sci. Technol.* **2010**, 44, 343-348.
(2) Russell, M. H.; Hoogeweg, G.; Webster, E. M.; Ellis D. A.; Waterland, R. L. *Environ. Toxicol. Chem.* (submitted)
(3) Baasandorj, M.; Ravishankara, A. R.; Burkholder, J. B. *J. Phys. Chem. A.* **2011**, 115, 10539-10549.

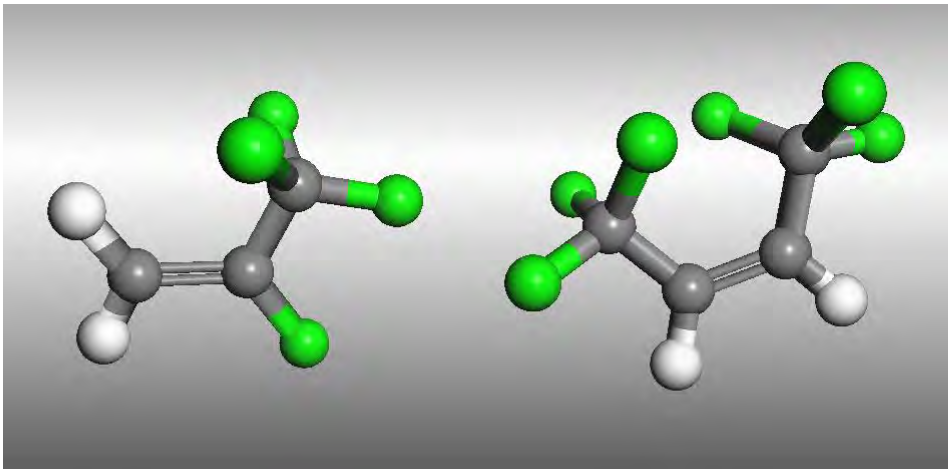


Figure. Structures of HFO-1234yf and the Z-isomer of HFO-1336mzz.

Understanding the Chemistry of Hydrofluoroolefin (HFO) Replacement Compounds: Cl Atom Kinetics and Adduct Formation

Shona C. Smith,[1,2,*] Munkhbayar Baasandorj,[1,2] and James B. Burkholder[1]

[1] National Oceanic and Atmospheric Administration (NOAA), Boulder, CO, USA
[2] Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO, USA
* Corresponding author: shona.smith@noaa.gov

Hydrofluorocarbons (HFCs) have been widely applied in various technologies, e.g. mobile air conditioning and foam blowing, as replacements for ozone depleting chlorofluorcarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). However, HFCs are, in general, potent greenhouse gases with high Global Warming Potentials (GWPs). Hydrofluoroolefins (HFOs) offer an alternative to their unsaturated predecessors where their high gas-phase reactivity leads to lower GWPs, thus, reducing their climate impacts. A thorough investigation of the atmospherically relevant chemical processing of these compounds is required in order to better understand their potential environmental impact.

Cl atom addition to the hydrofluoroolefins (HFOs) $CF_3CF{=}CH_2$ (2,3,3,3-tetrafluoropropene, HFO-1234yf) and (*Z*)-$CF_3CF{=}CHF$ (1,2,3,3,3-pentafluoropropene, HFO-1225ye) has previously been shown to, most likely, lead to the formation of a Cl-adduct that is semi-stable at 298 K or greater temperatures.[1,2] In this work, the Cl atom reaction with $CF_3CF{=}CH_2$ and (*Z*)-$CF_3CF{=}CHF$

$$\mathrm{Cl} + \mathrm{CF_3CF{=}CH_2} \leftrightarrow \mathrm{CF_3CFClC^{\bullet}H_2} \tag{1a}$$

$$\leftrightarrow \mathrm{CF_3C^{\bullet}FCH_2Cl} \tag{1b}$$

$$\mathrm{Cl} + (Z)\text{-}\mathrm{CF_3CF{=}CHF} \leftrightarrow \mathrm{CF_3CFClC^{\bullet}HF} \tag{2a}$$

$$\leftrightarrow \mathrm{CF_3C^{\bullet}FCHFCl} \tag{2b}$$

was studied over a range of temperature and pressure to further investigate the thermochemical parameters and reactivity of the Cl-adducts formed in reactions 1 and 2. Chlorine atoms were produced using pulsed laser photolysis of $(ClCO)_2$ or Cl_2 and its temporal profile measured using atomic resonance fluorescence (PLP-RF). Experiments were also performed with the addition of O_2 to the reaction mixture to determine the reactivity of the Cl-adducts with O_2. The results from this work are compared to earlier theoretical calculations from this group[1] and the indirect determinations from Kaiser *et al.*[2] for $CF_3CF{=}CH_2$.

References

(1) Papadimitriou, V.C.; Lazarou, Y.G.; Talukdar, R.J.; Burkholder, J.B. *J Phys. Chem. A.* **2011**, 115, 167-181.
(2) Kaiser, E.W.; Wallington, T.J. *J. Phys. Chem. A.* **2012**, ASAP.

Atmospheric degradation of two short-lived brominated hydrocarbons ($CHBr_3$ and CH_2Br_2)

G. Krysztofiak[1], G. Poulet[1], V. Marécal[2], M. Pirre[1], F. Louis[3], S. Canneaux[3] and V. Catoire[1,]*

[1] Laboratoire de Physique et Chimie de l'Environnement et de l'Espace (LPC2E), CNRS - Université d'Orléans (UMR 6115), 45071 Orléans cedex 2, France
[2] Centre National de Recherches Météorologiques- Groupe d'études de l'Atmosphère Météorologique (CNRM-GAME), Météo-France - CNRS (URA 1357), 31057 Toulouse cedex 1, France
[3] Physico Chimie des Processus de Combustion et de l'Atmosphère (PC2A) CNRS - Université Lille 1 Sciences et Technologies (UMR 8522), 59655 Villeneuve d'Ascq Cedex, France
*Corresponding author: Valery.Catoire@cnrs-orleans.fr

Two brominated VSLS, bromoform ($CHBr_3$) and dibromomethane (CH_2Br_2), which have natural sources in coastal regions, have the potential to transport reactive bromine into the stratosphere and to contribute to the bromine budget. In order to better evaluate the impact of these two species, chemical schemes for their atmospheric degradation have been developed from a detailed kinetic and mechanistic analysis of all the gas phase reactions involved, specially of the peroxy radicals. The most likely pathways for the reactions of HO_2 with brominated peroxy radicals RO_2 (with R = CH_2Br, $CHBr_2$ and CBr_3) have been established using *ab initio* calculations. The Henry's law constants of the brominated organics products have been also estimated using empirical methods. Using these constants, the less soluble species formed from the brominated VSLS degradation are found to be CBr_2O, CHBrO, $CBr_3O_2NO_2$, $CHBr_2O_2NO_2$, BrO, $BrONO_2$ and HOBr. In the presence of deep convection, these species could be transported into the TTL (tropical tropopause layer).

Then, these data have been implemented in a meteorological/tracer transport model (CATT-BRAMS), including a simplified chemistry of other atmospheric species The full degradation schemes have been run under realistic conditions of "clean" and moderately NO_x-polluted atmospheres, which are representative of tropical coastal regions. The influence of the reactions of the RO_2 radicals with HO_2, CH_3O_2 and NO_2 on the nature and abundance of the stable intermediate and end-products has been tested. In the case of $CHBr_3$ degradation, it results that the reactions of RO_2 with NO_2 have no impact, and that the inclusion of the reactions of RO_2 with CH_3O_2 and with HO_2 (with "new" branching ratios) leads to a slight decrease of the bromine potentially able to reach the TTL. In contrast to $CHBr_3$, the CH_2Br_2 degradation leads to a negligible production of organic species. Finally, for both bromoform and dibromomethane degradation, the effect of a moderate NO_x pollution significantly increases the production of the less soluble species and thus approximately doubles the bromine potentially able to reach the TTL. By taking into account the results of these analysis, simplified degradation schemes for $CHBr_3$ and CH_2Br_2 are proposed.

Kinetic studies of the $OH(X^2\Pi)$ and $O(^3P)$ initiated reactions with selected short chain iodoalkanes

Shaoliang Zhang,[1,2,3] Rafal S. Strekowski,[1,2,*] Anne Monod,[1,2] Sasho Gligorovski,[1,2] Henri Wortham,[1,2] Loïc Bosland,[2] and Cornelius Zetzsch[3]

[1] Aix-Marseille Univ., Laboratoire Chimie Environnement, 13331 Marseilles cedex 03, France
Tel: (+33) (0)4 13 55 10 40, Fax (+33) (0)4 13 55 10 60, E-mail: rafal.strekowski@univ-amu.fr
[2] CNRS, FRE 3416, 13331, Marseilles cedex 03, France
[3] Institut de Radioprotection et de Sûreté Nucléaire, DPAM / SEMIC / LETR, Cadarache, France
[4] Atmos. Chem. Research Lab, BAYCEER, University of Bayreuth, Dr.-Hans-Frisch-Str. 1-3, D-95448 Bayreuth, Germany

A Flash Photolysis–Resonance Fluorescence (FP-RF) technique was used to investigate the kinetics of the $OH(X^2\Pi)$ radical initiated reactions with selected iodoalkanes (RI), namely CH_3I, CH_2I_2, C_2H_5I, n-C_3H_7I, iso-C_3H_7I, CHI_3 and $O(^3P)$ radical initiated reactions with selected RI, namely CHI_3 and C_2H_5I. The reactions of $OH(X^2\Pi)$ radicals with RI were studied over the temperature range 295 – 390 K and pressure around 200 Torr of He.[1-3] The reaction of the $OH(X^2\Pi)$ radical with CHI_3 was studied at T=298K only. The reactions of $O(^3P)$ radical with CHI_3 and C_2H_5I were studied over the temperature range 296 – 373K in 14 Torr of He. The experiments involved time-resolved RF detection of OH ($A^2\Sigma^+ \rightarrow X^2\Pi$ transition at λ=308 nm) and of $O(^3P)$ (λ=130.2, 130.5, and 130.6 nm) following FP of the H_2O/He, H_2O/RI/He, O_3/He and O_3/RI/He mixtures. The $OH(X^2\Pi)$ and $O(^3P)$ radicals were produced by FP in the vacuum-UV at wavelengths λ>120 nm using a Xe flash lamp. Measured rate coefficients for the reactions of $OH(X^2\Pi)$ and $O(^3P)$ radicals with RI are described by the following Arrhenius expressions (units are $cm^3 molecule^{-1} s^{-1}$):

$$k_{\mathrm{OH+CH_3I}} = (4.1 \pm 2.2) \times 10^{-12} \exp[(-1240 \pm 200)\mathrm{K}/T]$$

$$k_{\mathrm{OH+CH_2I_2}} = (4.2 \pm 0.5) \times 10^{-11} \exp[(-670 \pm 20)\mathrm{K}/T]$$

$$k_{\mathrm{OH+CHI_3}} = (1.6 \pm 0.1) \times 10^{-11}$$

$$k_{\mathrm{OH+C_2H_5I}} = (5.6 \pm 3.2) \times 10^{-12} \exp[(-830 \pm 90)\mathrm{K}/T]$$

$$k_{\mathrm{OH+n-C_3H_7I}} = (1.7 \pm 0.9) \times 10^{-11} \exp[(-780 \pm 90)\mathrm{K}/T]$$

$$k_{\mathrm{OH+iso-C_3H_7I}} = (7.6 \pm 3.7) \times 10^{-12} \exp[(-530 \pm 80)\mathrm{K}/T]$$

$$k_{\mathrm{O+CHI_3}} = (1.8 \pm 2.8) \times 10^{-12} \exp[(+430 \pm 260)\mathrm{K}/T]$$

$$k_{\mathrm{O+C_2H_5I}} = (2.0 \pm 1.4) \times 10^{-11} \exp[(+140 \pm 110)\mathrm{K}/T]$$

The implications of the reported kinetic results for understanding the degradation mechanisms of iodoalkanes in case of a nuclear power plant accident are discussed. Further, the OH radical and O atom attacks on RI, namely OH-addition, H-atom and I-atom abstraction reaction channels, are discussed.

References

(1) S. Zhang, R. Strekowski , L. Bosland, A. Monod, Cornelius Zetzsch, Kinetic study of the reaction of OH with CH_3I revisited, *Int. J. Chem. Kinet.*, **2011**, 43, 547-556
(2) S. Zhang, R. Strekowski , L. Bosland, A. Monod, Cornelius Zetzsch, Kinetic study of the reaction of OH with CH_2I_2, *Phys. Chem. Chem. Phys.*, **2011**, 13, 11671-11677
(3) S. Zhang, R. Strekowski , L. Bosland, A. Monod, Cornelius Zetzsch, Temperature-Dependent Kinetics Study of the Reactions of OH with C_2H_5I, n-C_3H_7I and iso-C_3H_7I, *submitted to J. Phys. Chem. A*, **2012**

Kinetics with OH Radicals and Photochemistry of CF_3CF_2CHO

María Antiñolo,[1] Sergio González,[1] Elena Jiménez,[1,*] and José Albaladejo[1,*]

[1] University of Castilla-La Mancha, Facultad de Ciencias y Tecnologías Químicas, 13070 Ciudad Real, Spain
* Corresponding authors: Elena.Jimenez@uclm.es and Jose.Albaladejo@uclm.es

Ozone-friendly species hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) were reported to contribute in a great extent to the Earth's global warming.[1] Other non-depleting ozone substances, such as fluorinated alcohols (FA), have recently been proposed as substitutes. HCFCs, HFCs and FA are degraded in the troposphere yielding perfluorinated aldehydes, $C_xF_{2x+1}CHO$.[2,3] Perfluorinated aldehydes are thought to be precursors of perfluoroalkyl carboxylic acids (PFCAs, $C_nF_{2n+1}COOH$)[4]. Atmospheric removal of perfluorinated aldehydes is mainly initiated by reaction with OH radicals and sunlight. The aim of this work is to determine the ***OH-reaction rate coefficient*, k_{OH}**, for CF_3CF_2CHO as a function of temperature for the first time (T = 263 – 358 K) at different pressures (P = 50 – 205 Torr):

$$CF_3CF_2CHO + OH \rightarrow CF_3CF_2CO + H_2O$$

CF_3CF_2CHO was obtained from dehydration of $CF_3CF_2CH(OH)_2$ in the presence of P_2O_5 at 338 K and then stored in a stainless steel cylinder. OH radicals were generated by *pulsed laser photolysis* (PLP) of HNO_3(g) at 248 nm and subsequently probed to the first excited state by a frequency-doubled dye laser pumped by a Nd:YAG laser. *Laser induced fluorescence* (LIF) from OH radicals was detected by a filtered photomultiplier tube. Sulbaek Andersen et al.[4] previously determined the relative k_{OH} only at room temperature. At 275 K, the global temperature of the troposphere, k_{OH} was measured to be 4.8×10^{-13} cm^3 $molecule^{-1}$ s^{-1}, *i. e.*, its overall lifetime due to the OH-reaction is *ca.* 24 days. Additionally, the ***absorption cross sections*** ($\sigma_{\lambda=230\text{-}370\ nm}$) of CF_3CF_2CHO were determined as a function of temperature (269-323 K). The PLP technique was also used coupled to a Fourier transform infrared (FTIR) spectrometer to determine the ***photodissociation quantum yields*** of CF_3CF_2CHO ($\Phi_{\lambda = 308\ nm}$) as a function of total pressure (75-760 Torr in air). The overall loss of CF_3CF_2CHO and the formation of photooxidation end-products were monitored by FTIR spectroscopy. From our results, the main removal process for CF_3CF_2CHO in the atmosphere seems to be UV photolysis rather than reaction with OH.

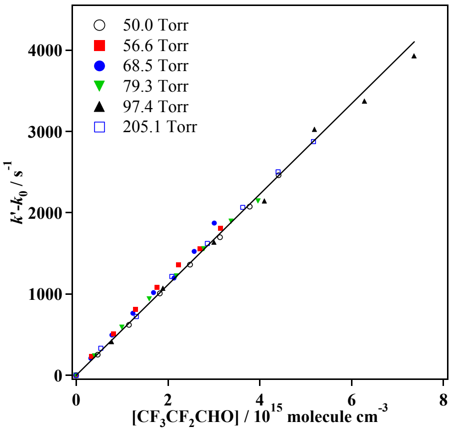


Fig. 1. *Pseudo*-first order plot at 298 K.

References

(1) Daniel, J.S.; Velders, G.J.M. (Lead Authors). Chapter 8 in *Scientific Assessment of Ozone Depletion: 2006,* Global Ozone Research and Monitoring Project - Report No. 50, WMO, **2007**.

(2) Hurley, M.D.; Wallington, T.J.; Sulbaek Andersen, M.P.; Ellis, D.A.; Martin, J.W.; Mabury, S.A.. *J. Phys. Chem. A* **2004**, 108, 1973-1979.

(3) Edney, E.O.; Driscoll, D.J. *Int. J. Chem. Kinet.* **1992**, *24*, 1067-1081.

(4) Sulbaek Andersen, M.P.; Hurley, M.D.; Wallington, T.J.; Ball, J.C.; Martin, J.W.; Ellis, D.A.; Mabury, S.A.; Nielsen, O.J. *Chem. Phys. Lett.* **2003**, 379, 28-36.

Kinetics of the Reactions of Atomic Chlorine with CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$

Patrick L. Laine,[1,2] J. Michael Nicovich,[3,*] Paul H. Wine,[1,3]
Yizhen Tang,[4] Arne J.C. Bunkan,[4] and Claus J. Nielsen[4]

[1] School of Earth & Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA, USA
[2] Now at Department of Earth & Atmospheric Sciences, University of Houston, Houston, TX, USA
[3] School of Chemistry & Biochemistry, Georgia Institute of Technology, Atlanta, GA, USA
[4] Department of Chemistry, University of Oslo, Oslo, Norway
* Corresponding author: mike.nicovich@chemistry.gatech.edu

Amines are thought to play an important role in secondary organic aerosol (SOA) formation in marine environments,[1] and atomic chlorine is a potentially important initiator of amine oxidation in such environments.[2] While one study of the dynamics and product branching ratio of the Cl + CH_3NH_2 reaction is reported in the literature,[3] there are no published kinetic data for any of the three title reactions. Using laser flash photolysis (LFP) studies of Cl kinetics in conjunction with supporting electronic structure calculations, we have investigated the kinetics of the three title reactions. In all experiments, atomic chlorine was generated by 248 nm LFP of phosgene (Cl_2CO). Dark reaction of amines with (presumably) HCl generated by hydrolysis of phosgene on the reactor walls was an experimental complication that had to be limited by careful choice of experimental conditions and dealt with in the data analysis. All three reactions studied are extremely fast, with measured 298 K rate coefficients ranging from 3.5 to 4.2×10^{-10} cm^3 $molecule^{-1}$ s^{-1}. Electronic structure calculations confirm that reaction proceeds via formation of pre-reactive complexes that dissociate to yield H-transfer products over barriers that lie below reactants in energy. Characteristic times for loss of marine boundary layer amines by reaction with Cl and OH[4-6] appear to be similar in magnitude.

Support for this research by the CO_2 Capture Mongstad Project (CCM), Norway is gratefully acknowledged.

References

(1) Sorooshian, A.; Padro, L.T.; Nenes, A.; Feingold, G.; McComiskey, A.; Hersey, S.P.; Gates, H.; Jonsson, H.H.; Miller, S.D.; Stephens, G.L.; Flagan, R.C.; Seinfeld, J.H. *Global Biogeochem. Cycles* **2009**, 23, GB4007.
(2) Laine, P.L., Nicovich, J.M.; Wine P.H. *J. Phys. Chem. A* **2011**, 115, 1658-1666, and references therein.
(3) Rudic, S.; Murray, C.; Harvey, J.N.; Orr-Ewing, A.J. *Phys. Chem. Chem. Phys.* **2003**, 5, 1205-1212.
(4) Atkinson, R.; Perry, R.A.; Pitts, J.N. Jr. *J. Chem. Phys.* **1977**, 66, 1578-1581.
(5) Atkinson, R.; Perry, R.A.; Pitts, J.N. Jr. *J. Chem. Phys.* **1978**, 68, 1850-1853.
(6) Carl, S.A.; Crowley, J.N. *J. Phys. Chem. A* **1998**, 102, 8131-8141.

Kinetics of the Gas-phase Reactions of OH Radicals and O_3 with Aliphatic Amines

Takamasa SETA, Kei SATO, and Takashi IMAMURA*

National Institute for Environmental Studies, Tsukuba, Ibaraki, JAPAN
* Corresponding author: imamura@nies.go.jp

Aliphatic amines emitted from a variety of sources into the atmosphere are removed by the gas-phase reactions as well as wet and dry deposition. Like other organic compounds, the reactions with OH radicals, ozone, and other reactive species would be possible removal processes of amines in the air. Therefore, their rate constants need to be obtained to estimate the atmospheric lifetimes of aliphatic amines. In this work, we have measured the rate constants for the gas-phase reactions of OH radicals (k_{OH}) and O_3 (k_{O3}) with N-methyl-ethanamine (MEA) and diethylamine (DEA) at 298 K and 760 Torr total pressure of air.

Experiments were conducted in a 6-m^3 evacuable photochemical reaction chamber. The concentration of reactants and products was measured by a long optical-path FTIR spectrometer. Prior to kinetic measurements, the decay in the concentration of the individual compounds ($k_{\mathrm{w}}^{\mathrm{A}}$) was measured in the chamber in the dark.

The kinetic measurements of the OH reactions were carried out in the amine–reference–NO–CH_3ONO–air photoirradiation system. The relative rate constant for the reactions of OH radicals with amines and the reference compounds was obtained from

$$\ln([\mathrm{amine}]_0/[\mathrm{amine}]_t) - k_{\mathrm{w}}^{\mathrm{A}} \times t = (k_{\mathrm{OH}}/k_{\mathrm{R}}) \times \ln([\mathrm{Ref}]_0/[\mathrm{Ref}]_t).$$

Here, k_{R} are the rate constant of OH reactions with reference compounds. Under our experimental conditions, the O-atom and O_3 reactions with amines and reference compounds were confirmed to have a negligible contribution to the OH kinetics. The obtained rate constants were summarized in Table 1.

The rate constants for the reactions of amines with O_3 were measured in the amine-O_3-CO-air system. Excess amount of CO was introduced to scavenge OH-radicals. The decay of amine was analyzed as

$$\ln([\mathrm{amine}]_0/[\mathrm{amine}]_t) = k_{\mathrm{O3}} \times \int[O_3]dt + k_{\mathrm{w}}^{\mathrm{A}} \times t.$$

The integration of the O_3 concentration over time was carried out numerically. The obtained rate constants were also summarized in Table 1.

Table 1. Summary of kinetic results and comparison with literature

amines	OH + amine reaction			O_3 + amine reaction	
	reference compound [a)]	k_{OH} / 10^{-10} [b)]		k_{O3} / 10^{-17} [b)]	
		this work	reference	this work	reference
$(CH_3)_2NH$	–	–	0.67 ± 0.05 [1,2]		0.17 ± 0.02 [4]
MEA	Pr, Isp, TMB	1.0 ± 0.2		0.65 ± 0.08	
DEA	Pr, Isp, TMB	1.3 ± 0.2	1.2 ± 0.3 [3]	1.6 ± 0.3	1.3 ± 0.2 [5]

[a)] Pr = propene, Isp = isoprene, TMB = 1,3,5-trimethylbenzene. [b)] Unit: cm^3 molecule^{-1} s^{-1}.

References

(1) Atkinson, R.; Perry, R.A.; Pitts, Jr., J.N. *J. Chem. Phys.* **1978**, 68, 1850-1853. (2) Carl, S.A.; Crowley, J.N. *J. Phys. Chem.* **1998**, 102, 8131-8141. (3) Tuazon, E.C.; Martin, P.; Aschmann, S.M.; Arey, J.; Atkinson, R. I*nt. J. Chem. Kinet.* **2011**, 43, 631-638. (4) Tuazon, E.C.; Atkinson, R.; Aschmann, S.M.; Arey, J. *Res. Chem. Intermed.* **1994**, 20, 303-320. (5) Gai, Y.-B.; Ge, M.-F., Wang, W.-G. *Acta Phys-Chim. Sin.* **2010**, 26, 1768-1772.

Atmospheric Oxidation of Amines Relevant for Carbon Capture and Storage

Lavinia C. Onel,[1,*] Mark A. Blitz,[1,†] and Paul W. Seakins[1]
[1] University of Leeds, Leeds, UK, † NCAS Fellow, * Corresponding author: chmlo@leeds.ac.uk

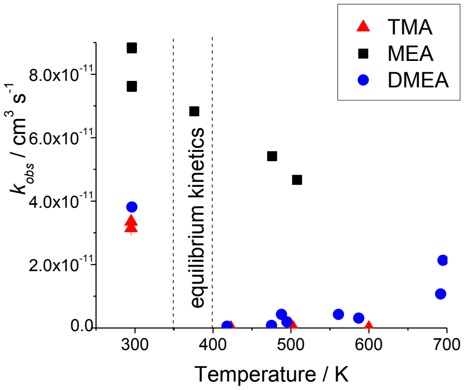
Amine-based compounds have been proposed for capturing CO_2 in Carbon Capture and Storage technology. However, in the case of large-scale CO_2 capture plants, there is potential for significant amine release to the atmosphere.[1] This study aims to fill in gaps in our knowledge about the atmospheric oxidation of such amines.

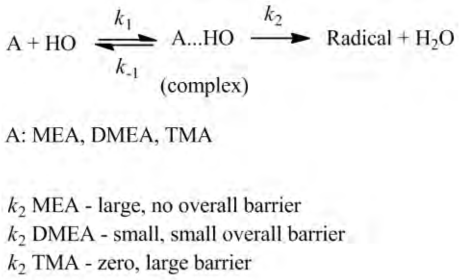
We have performed laser photolysis, laser induced fluorescence experiments on the reaction of OH radical with a range of amines: monoethanolamine (MEA, $H_2NCH_2CH_2OH$), dimethylethanolamine (DMEA, $(CH_3)_2NCH_2CH_2OH$) and trimethylamine (TMA, $(CH_3)_3N$). We have studied the decay of OH under pseudo-first-order conditions over the temperature range 296 – 700 K (Fig. 1). This is the first study on the temperature effect on these systems. We have found that all the amines initially form a weakly bonded complex with OH, k_1. In the case of MEA the formation of this complex is followed by a fast OH abstraction to products, k_2, at all temperatures (see Scheme 1). The value of the rate coefficient for the reaction of OH with MEA at 296 K is in a good agreement with that found very recently by Karl *et al*.[2] The reaction of DMEA with OH at room temperature is similarly characterized by a fast rate coefficient. However, at 380 K, equilibrium is observed, which is strong evidence for complex formation. Above 380 K, the reaction rate coefficient is much slower than at 296 K, but is increasing with temperature. In the case of TMA - OH system we observed similar behaviour except that, above the equilibrium temperature, no reaction is observed. The value of the rate coefficient for TMA - OH reaction at 296 K is in excellent agreement with that of Carl and Crowley.[3]

In order to find the site(s) for abstraction in these reactions between OH and amines we plan to perform further studies, using the same technique, by measuring OH kinetics with partially deuterated amines/methyl analogues and also to carry out product studies.

References

(1) Thitakamol, B.; Veawab, A.; Aroonwilas, A. *Int.J.Greenh.Gas Control* **2007**, 1, 318-342.
(2) Karl, M et al. *Atm.Chem.Phys.Disc.* **2011**, 11, 27763-27814.
(3) Carl, S. A.; Crowley, J. N. *J.Phys.Chem A* **1998**, 102, 8131-8141.





$$A + HO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A...HO \xrightarrow{k_2} \text{Radical} + H_2O$$

A: MEA, DMEA, TMA

k_2 MEA - large, no overall barrier
k_2 DMEA - small, small overall barrier
k_2 TMA - zero, large barrier

Scheme 1

Figure 1. Rate coefficients *vs*. temperature for the reaction of OH with: (■) monoethanolamine (MEA), (●) dimethylethanolamine (DMEA) and (▲) trimethylamine (TMA).

Spectroscopy of the simplest Criegee intermediate CH_2OO: Simulation of the first bands in its electronic and photoelectron spectra

Edmond P. F. Lee [a,b], Daniel K. W. Mok [b], Dudley E. Shallcross [c], Carl J. Percival [d], David L. Osborn [e], Craig A. Taatjes [e] and John M. Dyke [a]

[a] School of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, UK

[b] Department of Applied Biology and Chemical Technology, Hong Kong Polytechnic University, Hung Hom, Hong Kong

[c] School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, UK

[d] School of Earth, Atmospheric and Environmental Sciences, Centre of Atmospheric Science, University of Manchester, Oxford Road, Manchester M13 9PL, UK

[e] Combustion Research Faculty, Mail Stop 9055, Sandia National Laboratories, Livermore, California 94551-0969, USA

CH_2OO, the simplest Criegee intermediate, are isoelectronic with ozone. They both play very important roles in atmospheric chemistry. However, CH_2OO is much more reactive and there were no direct gas-phase studies until very recently when its photoionization efficiency spectrum was recorded and kinetics studies were made of some reactions of CH_2OO with a number of molecules of atmospheric importance, using photoionization mass spectrometry to monitor CH_2OO.

In order to encourage more direct studies on CH_2OO and other Criegee intermediates, the electronic and photoelectron spectra of CH_2OO have been simulated using high level electronic structure calculations and Franck-Condon factor calculations. Adiabatic and vertical excitation energies of CH_2OO were calculated with TDDFT, EOM-CCSD, and CASSCF methods. DFT, QCISD and CASSCF calculations were also performed on neutral and low-lying ionic states, with single energy calculations being carried out at higher levels to obtain more reliable ionization energies. The results show that the most intense band in the electronic spectrum of CH_2OO corresponds to the $\tilde{B}\,^1A' \leftarrow \tilde{X}\,^1A'$ absorption. It is a broad band in the region 250-450 nm showing extensive structure in vibrational modes involving O-O stretching and C-O-O bending. Evidence is presented to show that the electronic absorption spectrum of CH_2OO has probably been recorded in earlier work, albeit at low resolution. The results suggested that CH_2OO were prepared and observed in earlier work from the $CH_2I + O_2$ reaction and that the assignment of the observed spectrum solely to CH_2IOO was not correct.

The low ionization energy region of the photoelectron spectrum of CH_2OO consists of two overlapping vibrationally structured bands corresponding to one-electron ionizations from the highest two occupied molecular orbitals of the neutral molecule. In each case, the adiabatic component is the most intense and the adiabatic ionization energies of these bands are expected to be very close, at 9.971 and 9.974 eV at the highest level of theory used.

Hydrogen Peroxide Absorption at Long Wavelengths: Implications for HO_x Cycling

Tara F. Kahan,[1] R. A. Washenfelder,[2,3] V. Vaida,[1,3] and S. S. Brown[2*]

[1] University of Colorado, Boulder, CO, USA
[2] National Oceanic and Atmospheric Administration (NOAA), Boulder, CO, USA
[3] Cooperative Institute for Research in Environmental Sciences (CIRES), Boulder, CO, USA
* Corresponding author: Steven.S.Brown@noaa.gov

We have measured hydrogen peroxide (H_2O_2) absorption cross sections between 353 and 410 nm using incoherent broad-band cavity-enhanced absorption spectroscopy (IBBCEAS).[1] These measurements extend published electronic absorption cross sections by 60 nm, to absorption cross sections as low as 1×10^{-23} cm^2 $molecule^{-1}$. Photolysis rate constants calculated using these measurements at wavelengths longer than 350 nm as well as published cross sections at wavelengths shorter than 350 nm indicate that absorbance at longer wavelengths can account for up to 25% of H_2O_2 photolysis at high solar zenith angles. Loss of H_2O_2 via photolysis may be competitive with reactions with hydroxyl radicals and dry deposition in the lower atmosphere; these processes affect HO_x cycling very differently.

References

(1) Kahan, T.F.; Washenfelder, R.A.; Vaida, V.; Brown, S.S. *J. Phys. Chem. A* **2012**, in press.

Temperature Dependence of the Rate Constant and Product Studies for BrO + CH$_3$O+ using a Turbulent Flow Tube coupled to Chemical Ionisation Mass Spectrometry (CIMS)

Kimberley E. Leather[1], Asan Bacak[1], Dudley E. Shallcross[2] and Carl J. Percival[1]
[1]School of Earth, Atmospheric and Environmental Sciences, The University of Manchester, Williamson Building, Oxford Road, Manchester M13 9PL, UK
[2]School of Chemistry, University of Bristol, Bristol BS8 1TS, UK.
* Corresponding author: carl.percival@manchester.ac.uk

The importance of halogen chemistry in the atmosphere and its contribution to ozone depletion is widely recognised (Farman et al. 1985; Lary and Toumi, 1997). Bromine plays a major role in catalytic cycles leading to the destruction of ozone (Salawitch, 2009; Yang, 2005) not only in the stratosphere (Anderson et al., 1991) but also parts of the troposphere, in particular the marine boundary layer (Saiz-Lopez et al., (2006) as exemplified by the catalytic cycle below.

$Br + O_3 \rightarrow BrO + O_2$ (1)
$BrO + CH_3O_2 \rightarrow HOBr + CH_2O_2$ (2)
$HOBr + h\nu \rightarrow Br + OH$ (3)
$OH + CH_4 \rightarrow CH_3 + H_2O$ (4)
$CH_3 + O_2 \rightarrow CH_3O_2$ (5)
Net: $CH_4 + O_3 \rightarrow CH_2O_2 + H_2O$

Satellite measurements of BrO have been taken in northern and southern hemispheres (Simpson et al., 2007 and references therein). Gas-phase kinetic data exist for reaction of XO (BrO, ClO, IO) with O$_3$, NO$_x$ and HO$_x$ though there are limited data concerning the reaction of XO with CH$_3$O$_2$. In order to improve modelling of halogen related chemical processes leading to ozone depletion, the determination of reaction rates and product branching ratios is essential. Since the fates of BrO are not yet fully understood, a turbulent flow chemical ionisation mass spectrometer (CIMS) shall be employed to study the kinetics and product yields of the BrO + CH$_3$O$_2$ pathway. Experiments will be conducted for reaction (2) under pseudo first order conditions using very low radical concentrations, typically $(0.5 – 20) \times 10^{10}$ molecule cm^{-3}. Rate determinations will be retrieved as a function of atmospherically relevant temperatures (T = 180 – 300 K).

References

Anderson, J. G.; Toohey, D. W.; Brune, W. H. *Science* **1991**, 251, 39-46.
Farman, J. C.; Gardiner, B. G.; Shanklin, J. D. Nature **1985**, 315, 207-210.
Lary, D. J.; Toumi, R. *J. Geophys. Res.*, **1997**, 102, 23421-23428.
Saiz-Lopez, A.; Shillito, J. A.; Coe, H.; Plane, J. M. C. *Atmos. Chem. Phys.* **2006**, 6, 1513-1528.
Salawitch, R. J. *Nature* **2006**, 439, 275-277.
Simpson, W. R.; von Glasow, R.; Riedel, K.; Anderson, P.; Ariya, P.; Bottenheim, J.; Burrows, J.; Carpenter, L. J.; Friess, U.; Goodsite, M. E.; Heard, D.; Hutterli, M.; Jacobi, H. W.; Kaleschke, L.; Neff, B.; Plane, J.; Platt, U.; Richter, A.; Roscoe, H.; Sander, R.; Shepson, P.; Sodeau, J.; Steffen, A.; Wagner, T.; Wolff, E. *Atmos. Chem. Phys.* **2007**, 7, 4375-4418.
Yang, X.; Cox, R. A.; Warwick, N. J.; Pyle, J. A.; Carver, G. D.; O'Connor, F. M.; Savage, N. H. *J. Geophys. Res*. **2005,** 110, DOI10.1029/2005jd006244.

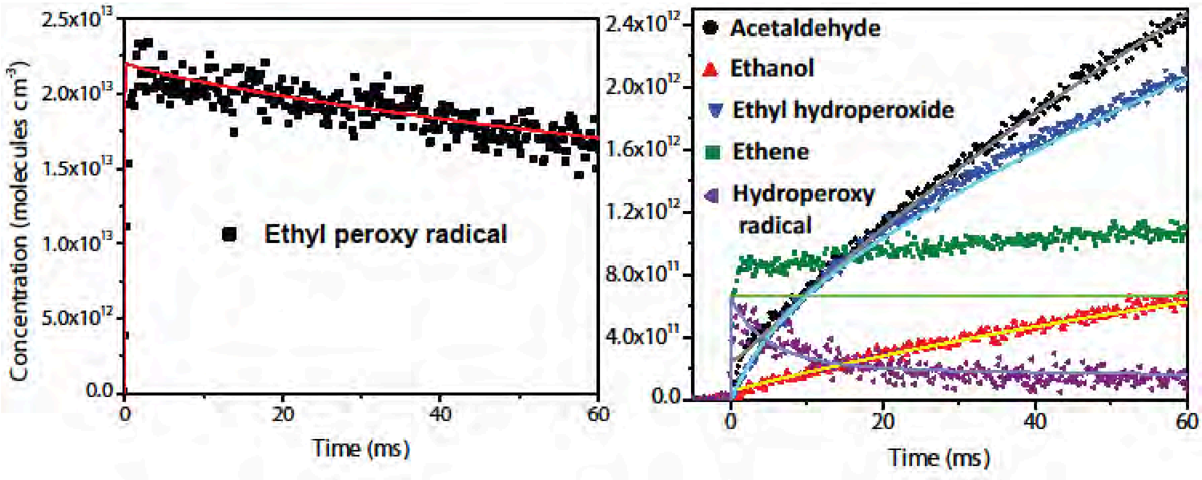
Kinetics and product branching ratio of the ethyl peroxy self-reaction

Nathan C. Eddingsaas,[1] John D. Savee,[2] Aaron C. Noell,[1] Leah G. Dodson,[1] Kana Takematsu,[1] Stanley P. Sander,[3] Craig Taatjes,[2] David L. Osborn[2] and Mitchio Okumura,[1,*]

[1] Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA
[2] Combustion Research Facility, Sandia National Lab, Livermore, CA, USA
[3] NASA Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA

* Corresponding author: mo@caltech.edu

Peroxy radicals (RO_2) are key intermediates in the reaction pathways of the oxidation of volatile organic carbon (VOCs) in the troposphere. RO_2 self- and cross-reactions can have two product channels, one forming reactive alkoxy radicals and another forming stable products (aldehydes and ketones), as well as suggestions that peroxides ROOR may be formed. These reactions are thought to proceed through tetroxide intermediates, but the mechanisms remain uncertain. In the atmosphere and in laboratory experiments, the radical channel can lead to secondary production of HO_2, further complicating kinetics measurements. We recently investigated the product branching ratio of the ethyl peroxy self-reaction using the NASA Jet Propulsion Laboratory Infrared Kinetics Spectroscopy experiment and found substantially lower radical yields than indicated from end product studies. Here we report new results on the kinetics and product yields of the ethyl peroxy radical reaction using the Sandia Combustion Research Facility multiplexed photoionization mass spectrometry apparatus. These experiments use VUV light from synchrotron radiation from the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory. This technique has allowed us to observe the concentration of the reactants, reactive intermediates, and end products in real time. In addition to kinetics and product branching ratios, we have determined the photoionization cross sections of HO_2 and H_2O_2 and a lower bound for the rate constant of the reaction of ethyl peroxy and ethoxy radicals.



Fig

Figure 1. Time traces of reactants, radical intermediates and products of the ethyl peroxy self-reaction.

Direct detection and kinetics of NO_3 and Cl-substituted alkylperoxy radicals using cavity ringdown spectroscopy

Leah G. Dodson, Kana Takematsu, Nathan C. Eddingsaas, and Mitchio Okumura[1,*]

[1] California Institute of Technology, Pasadena, CA, USA
* Corresponding author: mo@caltech.edu

Peroxy radicals dominate atmospheric chemistry as important reaction intermediates in the oxidation of volatile organic compounds. Biogenic alkene emissions such as isoprene and 2-methyl-3-buten-2-ol (MBO-232) react rapidly with free radicals to form β-substituted alkylperoxy radicals. We have directly detected the A-X electronic transition spectrum of NO_3- and Cl-substituted atmospherically-relevant alkyl peroxy radicals from 7000-8500 cm^{-1} using cavity ringdown spectroscopy. Spectra of peroxy radicals formed by NO_3 and Cl radical-initiated oxidation of 2-butene, 3-methyl-1-butene, and MBO-232 are presented here with preliminary kinetic results. Kinetic rate constants of peroxy radical self-reactions and peroxy radical reactions with HO_2 and NO will be obtained by directly observing the near-infrared absorption spectrum of the peroxy radical intermediate. The preliminary Cl-substituted isoprenyl peroxy radical A-X electronic transition spectrum has also been obtained.

Temperature-dependent rate constants of regular and fully-deuterated methoxy radical reacting with O_2

Hongyi Hu,[1] Theodore S. Dibble,[1,*] Geoffrey S. Tyndall,[2,*] and John J. Orlando[2]

[1] Chemistry Department, State University of New York College of Environmental Science and Forestry (SUNY-ESF), 1 Forestry Drive, Syracuse, USA
[2] Atmospheric Chemistry Division, National Center for Atmospheric Research (NCAR), Boulder, CO, USA
* Corresponding author: tsdibble@esf.edu, tyndall@ucar.edu

The methoxy radical is an intermediate in the atmospheric oxidation of methane, and as the simplest alkoxy species, its behavior is fundamental to understanding the degradation of alkoxy radicals. The temperature-dependent rate constants for methoxy radicals reacting with O_2 have been studied both experimentally and theoretically. However, all previous experiments were carried out at room temperature and above, which may fail to represent the situation in the atmosphere. Furthermore, the mechanism of this fundamental reaction remains uncertain: the fitted experimental Arrhenius equation suggests a small pre-exponential factor (10^{-14} $cm^3 molecule^{-1} s^{-1}$), and previous theoretical studies suggest that tunneling effects play a significant role in this reaction. The rate constants of CD_3O (the fully deuterated isotopologue of CH_3O) with O_2 are expected to be much smaller due to zero-point energy effects and the reduced tunneling effect, which may provide insights into the mechanism of the reaction.

Using the FT-IR smog chamber technique, we measured the relative rate constants of CH_3O reacting with O_2 and NO_2 at 250-333 K, as well as the relative rate constants of CD_3O reacting with O_2 and NO_2 at 277-335 K. Applying the IUPAC recommended rate constants of CH_3O and NO_2, the absolute rate constants of CH_3O and CD_3O reacting with O_2 are fitted (see the attached plot) by the Arrhenius expression, giving $k_{CH_3O+O_2} = 1.89^{+0.89}_{-0.60} \times 10^{-14} \exp[-(751 \pm 107)/T]$ $cm^3 molecule^{-1} s^{-1}$; $k_{CD_3O+O_2} = 2.58^{+1.57}_{-0.98} \times 10^{-15} \exp[-(667 \pm 145)/T]$ $cm^3 molecule^{-1} s^{-1}$, respectively. Over the range 277-333 K, the kinetic isotope effect associated with deuterium substitution is about 5, and not sensitive to temperature.

References

(1) Orlando, J.J.; Tyndall, G.S.; Wallington, T.J. *Chem. Rev.* **2003**, 103, 4657-4689.

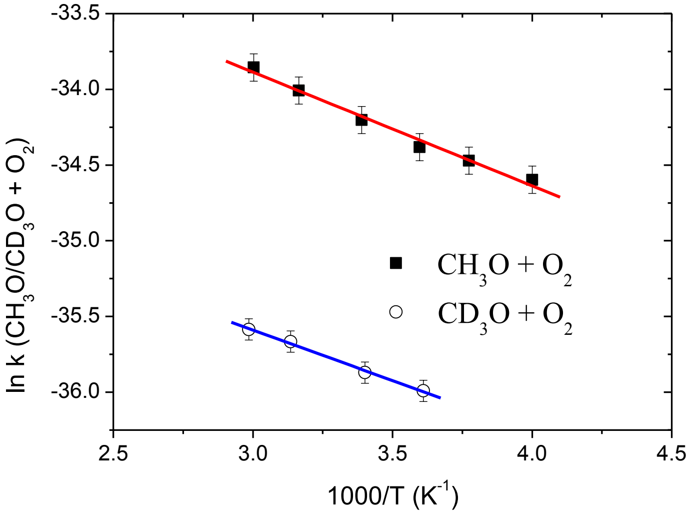


Figure 1: Fitted Arrhenius plot of the temperature-dependent rate constants of the two title reactions: $CH_3O + O_2$ and $CD_3O + O_2$.

Studies of the gas phase reactions of linalool, 6-methyl-5-hepten-2-ol and 3-methyl-1-penten-3-ol with O_3 and OH radicals

F. Bernard,[1] V. Daële,[1] A. Mellouki,[1,*] and H. Sidebottom[2]

[1] ICARE-CNRS and OSUC, Orléans, France
[2] School of Chemistry and Chemical Biology, University College Dublin, Ireland
* Corresponding author: mellouki@cnrs-orleans.fr

The reactions of three unsaturated alcohols (linalool, 6-methyl-5-hepten-2-ol and 3-methyl-1-penten-3-ol) with ozone and OH radicals have been studied using simulation chambers at T ~ 296 K and P ~ 760 Torr. The rate coefficient values (in cm^3 $molecule^{-1}$ s^{-1}) determined for the three compounds are: linalool, $k_{O3} = (4.1 \pm 1.0) \times 10^{-16}$ and $k_{OH} = (1.7 \pm 0.3) \times 10^{-10}$; 6-methyl-5-hepten-2-ol, $k_{O3} = (3.8 \pm 1.2) \times 10^{-16}$ and $k_{OH} = (1.0 \pm 0.3) \times 10^{-10}$; 3-methyl-1-penten-3-ol, $k_{O3} = (5.2 \pm 0.6) \times 10^{-18}$ and $k_{OH} = (6.2 \pm 1.8) \times 10^{-11}$. From the kinetic data it is estimated that for the reaction of O_3 with linalool, attack at the R-CH=C(CH_3)$_2$ group represents around (93 ± 52)% ($k_{\text{6-methyl-5-hepten-2-ol}}/k_{\text{linalool}}$) of the overall reaction with reaction at the R-CH=CH_2 group accounting for about (1.3 ± 0.5)% ($k_{\text{3-methyl-1-penten-3-ol}}/k_{\text{linalool}}$). In a similar manner it has been calculated that for the reaction of OH radicals with linalool, attack of the OH radical at the R-CH=C(CH_3)$_2$ group represents around (59 ± 18)% ($k_{\text{6-methyl-5-hepten-2-ol}}/k_{\text{linalool}}$) of the total reaction while addition of OH to the R-CH=CH_2 group is estimated to be around (36 ± 6)% ($k_{\text{3-methyl-1-penten-3-ol}}/k_{\text{linalool}}$).

Analysis of the products from the reaction of O_3 with linalool confirmed that addition to the R-CH=C(CH_3)$_2$ group is the predominant reaction pathway. The presence of formaldehyde and hydroxyacetone in the reaction products together with compelling evidence for the generation of OH radicals in the system, indicates that the hydroperoxide channel is important in the loss of the biradical $[(CH_3)_2COO]^*$ formed in the reaction of O_3 with linalool. Studies on the reactions of O_3 with the unsaturated alcohols showed that the yields of SOA are higher in the absence of OH scavengers compared to the yields in their presence. However, even under low-NO_X concentrations, the reactions of OH radicals with 3-methyl-1-pentene-3-ol and 6-methyl-5-hepten-2-ol will make only a minor contribution to SOA formation under atmospheric conditions. Relatively high yields of SOA were observed in the reactions of OH with linalool although the initial concentrations of reactants were quite high. The importance of linalool in the formation of SOA in the atmosphere requires further investigation. The impact following releases of these unsaturated alcohols into the atmosphere are discussed.

Rate of degradation of $CH_3CH{=}CHC(O)OCH{=}CH_2$ and $CH_3C(O)OCH{=}CHCH{=}CH_2$ in the troposphere

M. B. Blanco,[1,2] I. Barnes,[1*] I. Bejan[1] and P. Wiesen[1]

[1] Physikalische Chemie/FBC, Bergische Universität Wuppertal, 42119 Wuppertal, Germany.
[2] Instituto de Investigaciones en Fisicoquímicas de Córdoba (INFIQC), Dpto. de Fisicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba. Ciudad Universitaria, 5000 Córdoba, Argentina.
* Corresponding author: barnes@uni-wuppertal.de

Primary volatile organic compounds (VOCs) are emitted into the atmosphere from anthropogenic and biogenic (natural) sources. The fate and persistence of VOCs in the atmosphere is largely determined by their reactivity with different oxidant species present in the troposphere (generally OH radicals, NO_3 radicals and O_3 molecules). These reactions play an important role in determining the oxidation capacity and chemistry of the lower troposphere.[1]
The unsaturated esters vinyl crotonate ($CH_3CH{=}CHC(O)OCH{=}CH_2$) and 1-acetoxy-1,3-butadiene ($CH_3C(O)OCH{=}CHCH{=}CH_2$) are widely used in the production of polymers. Their copolymers are brittle resins, but they are used as cross-linking agents for other resins to raise the softening point and to increase abrasion resistance.[2,3] The widespread industrial use of these esters on a large scale unavoidably results in fugitive emissions of the compounds to the atmosphere.
As part of ongoing work to ascertain the atmospheric chemistry of esters, rate coefficients for the gas-phase reactions of vinyl crotonate and 1-acetoxy-1,3-butadiene with OH and NO_3 radicals and O_3 have been measured using a relative kinetic method. All the experiments were performed at room temperature (298±2 K) and atmospheric pressure in a 480 l cylindrical borosilicate glass photoreactor and in situ FTIR analysis was used to monitor the concentration-time behavior of the esters and the hydrocarbon reference compounds.[3] The *trans* isomer of vinyl crotonate was investigated whereas the sample of 1-acetoxy-1,3-butadiene was a mixture of *trans* and *cis* isomers.
The following rate coefficients (in units of $cm^3\ molecule^{-1}s^{-1}$) have been obtained for the reactions of vinyl crotonate with the oxidants: $k_{OH} = (4.49 \pm 1.05) \times 10^{-11}$, $k_{NO3} = (2.12 \pm 0.53) \times 10^{-14}$ and $k_{O3} = (0.98 \pm 0.34) \times 10^{-17}$. For the corresponding reactions of 1-acetoxy-1,3-butadiene the following values were obtained: $k_{OH} = (9.07 \pm 0.30) \times 10^{-11}$, $k_{NO3} = (3.17 \pm 0.57) \times 10^{-14}$ and $k_{O3} = (2.71 \pm 0.64) \times 10^{-17}$.
To the best of our knowledge, this work represents the first experimental kinetic study of the reactions of OH and NO_3 radicals and O_3 molecules with vinyl crotonate and 1-acetoxy-1,3-butadiene. The kinetic data will be presented and discussed in terms of reactivity trends for reactions of atmospheric oxidants with unsaturated compounds. The implications of the results for the fate of the esters in the troposphere will also be addressed.

References

(1) Finlayson-Pitts, B. J.; Pitts , J. N. Jr. *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications* **2000**, Wiley, New York.
(2) Su, T.; Liao, J.; Guo, L.; La, M. *Technology Development Chemical Industry*, **2007**, 3, 26-29.
(3) www.basf.com
(4) Barnes, I.; Becker, K.H.; Mihalopoulos, N. *J. Atmos. Chem.* **1994**, 18, 267-289.

Kinetic study of butenedial with the main atmospheric oxidants

P. Martín, I. Colmenar, B. Cabañas, M. S. Salgado, E. Martínez and A. Tapia.

Departamento de Química Física, Facultad de Ciencias Químicas, Universidad de Castilla La Mancha.
Avda Camilo José Cela 10, 13071 Ciudad Real (Spain).

Butenedial, (OHCCH=CHCHO), has been identified as a primary product from the reaction of furan with the main atmospheric oxidants, chlorine(1), OH (2) and NO_3 (3) Butenedial has also been detected after the OH photo-oxidation of reactive aromatic compounds such as toluene and o-xylene(4).
The degradation reactions of trans-2-butenedial with OH, NO_3 radicals and Cl atoms were investigated using a relative rate method. The experiments were carried out at ~298 ± 1 K and atmospheric pressure of N_2 or synthetic air as bath gas. Two different sampling/detection methods have been used for the study with Cl and OH: (1) Solid-Phase Microextraction and gas chromatography with flame ionization detection (SPME/GC-FID) and (2) "in situ" with long path Fourier Transform Infrared Spectroscopy (FTIR). In the case of NO_3 study Tenax solid adsorbent was used as sampling method and gas chromatography with Mass Spectrometry (GC-MS) as detection system. The measured rate coefficients for E-2-butenedial (cm^3 $molecule^{-1}$ s^{-1}) are: $(1.20 \pm 0.28\ ) x10^{-10}$ for Cl atoms, $(3.44 \pm 0.30)x10^{-11}$ for OH radical and $(1.77 \pm 0.72)\ x10^{-15}$ for NO_3 radical. For the reaction of Cl and NO_3 these are the first data of rate coefficients and in the case of OH the literature value was confirmed(5). The results confirm that the chemical characteristics of the organic substances have a limited influence on the reactivity with Cl, a larger effect in the OH-case but are decisive for the NO_3 reactions. Calculated atmospheric lifetime with each atmospheric oxidant is 8 days and 8 hours for Cl and OH respectively. In the case of Cl atoms a lifetime of 19 hours is estimated in the early morning hours in urban coastal air.

1. Villanueva F, Barnes I, Monedero E, Salgado S, Gómez V and Martín P, *Atmospheric Environment,* **2007**, 41, 8796.
2. Gómez-Álvarez E, Borrás E, Viidanoja J and Hjorth J, *Atmospheric Environment,* **2009**, 43, 1603.
3. Berndt T, Böge O and Rolle W, *Environmental Science Technology,* **1997**, 31, 1157.
4 Arey J, Obermeyer G, Aschamann S. M, Chattopadhyay S, Cusick R D. and Atkinson R *Environmental Science Technology,* **2009**, 43, 683.
5. Bierbach A, Barnes I, Becker K.H and Wiesen E, *Environmental Science and Technology*, **1994**, 28 (4), 715.

OH from reactions of HO_2 with organic peroxy radicals (RO_2)

Christoph Groß,[1,*] Terry Dillon,[1] and John Crowley[1]

[1] Max-Planck-Institut für Chemie, Mainz, Germany.
* Corresponding author: christoph.gross@mpic.de

The OH yield (α) of the reactions of HO_2 with twelve different RO_2 has been determined experimentally using Pulsed Laser Photolysis (PLP) combined with Laser Induced Fluorescence (LIF) and Transient Absorption Spectroscopy (TAS). Direct measurement of the main species OH, HO_2, RO_2 and O_3 enabled extraction of α via numerical simulation of their time dependent concentration profiles.

$HO_2 + RO_2$ ---> $HO + RO + O_2$ R1a
$ROH + O_3$ R1b
$RO_2H + O_2$ R1c

A wide range of RO_2 was investigated, including ones with oxo-, hydroxy-, fluoro- and aromatic substituents. We found the highest values of α (larger than 70%) for RO_2 bearing a carbonyl group close to the peroxy entity.

Is OH produced from NO_2^* + H_2O or NO_3^* + H_2O?

Terry J. Dillon [1,*] and John N. Crowley

[1] Max Planck Institute for Chemistry, Mainz, Germany
* Corresponding author: terry.dillon@mpic.de

Li *et al.* (1) identified a new source of atmospheric radicals, whereby electronically excited NO_2 (A^2B_2 or B^2B_1, together denoted NO_2^*, produced via photoexcitation, R1), reacts with H_2O to generate OH (R2b):

$$
\begin{array}{llll}
NO_2 + h\nu \text{ (vis.)} & \rightarrow & NO_2^* & (R1) \\
NO_2^* + H_2O & \rightarrow & NO_2 + H_2O & (R2a) \\
 & \rightarrow & OH + HONO & (R2b)
\end{array}
$$

Despite the reportedly low product yield, $k_{2b} / k_2 = 0.001$, this process may still represent a significant source of OH due to the large solar flux in the visible region of the spectrum. Wennberg et al. (2) calculated enhancements in modeled OH of up to 40 % upon including (R1-R2) in polluted-air scenarios. Large uncertainties remain however, as several groups (3,4,5) have found little or no evidence for OH production following excitation at certain discrete visible wavelengths.

Accordingly, experiments were conducted using pulsed laser excitation at five suitable visible wavelengths (532 – 647 nm) to prepare NO_2^*. Despite the presence of a large excess of H_2O, no evidence for OH formation (R1b) was found. Calibration of the LIF detection system allowed upper-limits of $k_{2b} / k_2 < 0.0002$ to be assigned at all wavelengths tested, indicating that this reaction is of no atmospheric interest.

The experimental setup was extended to facilitate generation of NO_3 radicals by pulsed laser photolysis. Pulsed laser excitation (R3, 612 – 662 nm) was used to generate excited-state radicals NO_3^* ($A^2\Sigma$); calibrated LIF to monitor any OH production from (R4).

$$
\begin{array}{llll}
NO_3 + h\nu \text{ (vis.)} & \rightarrow & NO_3^* & (R3) \\
NO_3^* + H_2O & \rightarrow & NO_3 + H_2O & (R4a) \\
 & \rightarrow & OH + HONO_2 & (R4b)
\end{array}
$$

T
H
U
R
S
D
A
Y

References

(1) Li, S.; Matthews, J.; Sinha, A. *Science* **2008,** 319, 1657.
(2) Wennberg, P.O.; Dabdub, D. *Science* **2008,** 319, 1624.
(3) Crowley, J.N.; Carl, S.A. *J. Phys. Chem. A.* **1997**, 101, 4178.
(4) Carr, S.; Blitz, M.A.; Heard, D.E. *Science* **2009**, 324, 336.
(5) Amédro, D.; Parker, A. E.; Schoemaecker, C.; Fittschen, C. *Chem. Phys. Lett.* **2011**, 513, 12.

A kinetic study of the gas phase reaction between HO_2 radicals and HCHO

Pranay Morajkar[1], Coralie Schoemaecker[1], Mitchio Okumura[2] and Christa Fittschen[1]*

[1]University Lille, Villeneuve d'Ascq, France
[2]Department of Chemistry, California Institute of Technology CA 91125, USA
* Corresponding author: Christa.Fittschen@univ-lille1.fr

Formaldehyde (HCHO) is an important indicator of tropospheric hydrocarbon emissions and photochemical activity. It is a principal intermediate in the oxidation of hydrocarbons in the troposphere. Hence it is considered as an important compound for determining the oxidative capacity of the atmosphere. The mechanism by which formaldehyde is photo-oxidized in the troposphere has been the subject of many investigations. It is well understood that the photolysis of formaldehyde occurs according to one of the following two pathways (R1) and (R2) and the subsequent reaction of H and HCO with O_2 produces HO_2 radicals.

$$HCO + h\nu \rightarrow H_2 + CO \qquad (R1)$$
$$\rightarrow H + HCO \qquad (R2)$$
$$H + O_2 \rightarrow HO_2 \qquad (R3)$$
$$HCO + O_2 \rightarrow HO_2 + CO \qquad (R4)$$

The reaction of HO_2 radicals with carbonyl compounds has been proposed as a major sink for carbonyl compounds in the Upper Troposphere / Lower Stratosphere (UTLS). These reactions proceed through a hydrogen bound intermediate before isomerizing into a hydroxyalylperoxy radical. Formaldehyde serves as a prototype for this class of reaction:

$$HO_2 + CH_2O \leftrightarrow HO_2CH_2O \leftrightarrow O_2CH_2OH \qquad (R5)$$

Previous measurements of this equilibrium have used either FTIR spectroscopy of end products [1] or via absorption of the B-X band of the direct reaction product, hydroxymethylperoxy (HMP) [2, 3]. However, theses measurements are fairly indirect and might have been affected by possible interferences from other species (HO_2, CH_3O_2) within the structure less B-X transition of HMP. Recent results [4] have directly detected HMP on the A-X electronic transition and on the ν_1 vibrational OH stretch transition using CRDS. They have found considerable disagreements with the above mentioned literature values.

In this work we will present direct measurements of the equilibrium (R5) through a selective and sensitive detection of HO_2 radicals by cw-CRDS coupled to laser photolysis. The CH_2O concentration was determined from the known rate constant of its reaction with OH, i.e. through measurement of the pseudo-first order decay of OH radicals by LIF. CH_2O concentrations could also be determined by direct measurement of their absorption in the near IR by cw-CRDS.

References

[1] Su, F., J.G. Calvert, J.H. Shaw *J. Phys. Chem.,* **1979**, *83*(25), 3185-3191
[2] Burrows, J.P., G.K. Moortgat, G.S. Tyndall, R.A. Cox, M.E. Jenkin, G.D. Hayman, B. Veyret *J. Phys. Chem.*, **1989**, *93*(6), 2375 - 2382.
[3] Veyret, B.; Lesclaux, R.; Rayez, M-T.; Rayez, J-C.; Cox, R.A.; Moortgat, G.K. *J. Phys. Chem*., **1989**, 93, 2368 – 2374.
[4] Sprague M.K., S.P. Sander and M. Okumura, Poster at GK **2010** in Leuven

Kinetics of reactions of Cl atoms with C4 – C5 hydrocarbons over a temperature range of ~220 – 320 K

Luke N. Farrugia[1*], Fred Winiberg[1], Dwayne E. Heard[1], Paul W. Seakins[1].

[1] University of Leeds, UK
* Corresponding author: cmlnf@leeds.ac.uk

Chlorine has been traditionally associated with marine boundary layer chemistry, however recent observations of high [$ClNO_2$] in inland urban areas in the USA (1), as well as significant [Cl] in volcanic plumes in Iceland, have had an impact on the importance of chlorine chemistry outside the marine environment.

Several room temperature relative-rate ratios have been reported for *n*-butane and iso-butane, differing by 20% between different authors, with some studies performed over high temperature ranges but only one reported over low temperatures. Very few previous studies have focused on Cl reactions with *n*-pentane and iso-pentane at 298 K and to our knowledge no previous temperature dependent studies have been reported for these alkanes. Reactions of Cl atoms with a set of non-methane hydrocarbons (NMHCs): *n*-butane, iso-butane, *n*-pentane and iso-pentane were studied experimentally using the Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC) (2).

Relative-rate experiments were carried out over a temperature range of 220 – 320 K at 760 Torr. FTIR and GC were used to measure rate coefficients for the Cl + NMHC reactions using an ethane reference. Relative-rate ratios obtained at 298K for all NMHCs investigated are in good agreement with recent literature data. Low temperature relative-rate ratios obtained using both GC and FTIR were in excellent agreement with each other in contrast to some previous studies. Site-specific rate data will be determined for these NMHCs and product branching fractions using deuterated compounds are planned for Cl atom reactions with other NMHCs to obtain an insight into product ratios and mechanistic information of these reactions.

References

(1) Thornton, J. A. et al., Nature, 464, pp.271-274, **2010**.
(2) Glowacki, D. R. et al., Atmos. Chem. Phys., 7, pp.5371-5390, **2007**.

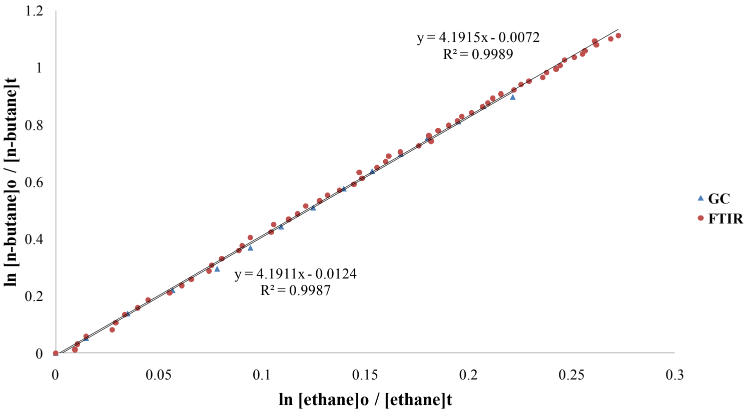


Fig.1.: Comparison of GC and FTIR relative-rate plots for Cl + n-butane using ethane reference at 298 K determined by GC (4.1911, ▲) and FTIR (4.1915, ●).

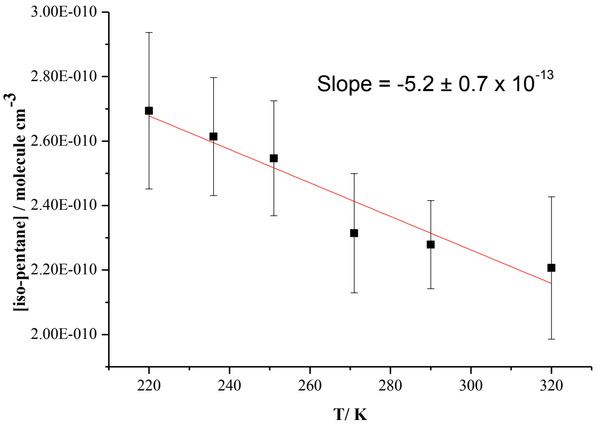


Fig.2.: Rate coefficient for Cl + iso-pentane against temperature.

The Kinetics of the Gas-phase Reactions of Selected Monoterpenes and Cyclo-alkenes with Ozone and the NO_3 Radical.

D.J. Stewart[*], S.H. Almabrok, J.P. Lockhart, O.M. Mohamed, D.R. Nutt, C. Pfrang and G. Marston

Department of Chemistry, University of Reading, Whiteknights, PO Box 224 Reading, RG6 6AD

The relative rate method has been used to measure the room-temperature rate constants for the gas-phase reactions of ozone and NO_3 with selected monoterpenes and cyclo-alkenes with structural similarities to monoterpenes. Measurements were carried out at 298 ± 2 K and 760 ± 10 Torr. The following rate constants (in units of 10^{-18} cm^3 $molecule^{-1}$ s^{-1}) were obtained for the reaction with ozone: methyl cyclohexene (132±15), terpinolene (1250±325), ethylidene cyclohexane (222±57), norbornene (959±249), t-butyl isopropylidene cyclohexane (1510±200), cyclopentene (546±61), cyclohexene (81.8±10.5), cyclooctene (454±45), dicyclopentadiene (1460±150) and α-pinene (95.5±9.8). For the reaction with NO_3 the rate constants obtained (in units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}) were: methyl cyclohexene (7.91±0.76), terpinolene (46.9±5.1), ethylidene cyclohexane (4.39±0.30), norbornene (0.27±0.02), cyclohexene (0.54±0.02), cyclooctene (0.52±0.02), dicyclopentadiene (1.21±0.06) and α-pinene (5.20±0.32). Molecular orbital energies were calculated for each alkene and the rate data are discussed in terms of the deviation from the structure-activity-relationship obtained from the rate constants for a series of simple alkenes. Lifetimes with respect to key initiators of atmospheric oxidation have been calculated suggesting that the studied reactions play dominant roles in the night-time removal of these compounds from the atmosphere.

The Regional Atmospheric Chemistry Mechanism

William R. Stockwell,[1] Charlene V. Lawson,[2] and Wendy S. Goliff[3,*]

[1] Howard University, Department of Chemistry, Washington, DC, USA
[2] Howard University, Department of Chemistry, Washington, DC, USA
[3] University of California, Center for Environmental Research and Technology, Riverside, California, USA
* Corresponding author: William.R.Stockwell@Gmail.com

Models such as the Community Multi-scale Air Quality Model (CMAQ) and the Weather Research and Forecasting Model with Chemistry WRF/CHEM are used by NOAA and EPA for air quality forecasting. The new Regional Atmospheric Chemistry Mechanism, version 2, (RACM2) has been developed for implementation in these models. The mechanism is being tested against chamber experiments performed at the University of California, Riverside, and against field observations made at Howard University's Beltsville Center for Climate System Observation (BCCSO) and the Desert Research Institute in Reno, NV. It is likely that the RACM2 approach to the organic chemistry will provide better forecasts of the production of aerosol from organic compounds. The Carbon Bond mechanism loses much information on the number of carbon atoms in the precursor molecules but this information is retained to a greater degree in RACM2.

References

(1) Stockwell, W.R.; Lawson, C.V.; Saunders, E.; Goliff, W.S., *Atmosphere*. **2012**, 3, 1-32.

The Effects of Daytime and Nighttime Chemistry on Air Quality Forecasts

Charlene V. Lawson,[1] William R. Stockwell,[2] and Wendy S. Goliff[3,*]

[1] Howard University, Department of Chemistry, Washington, DC, USA
[2] Howard University, Department of Chemistry, Washington, DC, USA
[3] University of California, Center for Environmental Research and Technology, Riverside, California, USA
* Corresponding author: cvlawson@howard.edu

NOAA's air quality forecast program focuses on tropospheric ozone and aerosol because these pollutants have significant effects on human health. Nitric oxide and nitrogen dioxide together are known as NO_x. NO_x is an important precursor to ozone and aerosol formation and processes that affect NO_x concentrations will have a strong effect on daytime ozone and aerosol formation. Measurements of NOx and organic compounds have been made at Howard University's Beltsville Center for Climate System Observation (BCCSO) and the Desert Research Institute in Reno, NV. The Regional Atmospheric Chemistry Mechanism, version 2 (RACM2) and other mechanisms are being used to model these field measurements. The gas-phase chemical mechanism is an essential component for air quality forecast models. Process analysis and sensitivity analysis are used to calculate the response of ozone and aerosol to variations in the mechanisms and to emissions. Comparisons between measurements and RACM2 forecasts and between the forecasts made with other mechanisms are being used to refine the RACM2 mechanism. The results of these studies will be presented.

Reference

(1) Stockwell, W.R.; Lawson, C.V.; Saunders, E.; Goliff, W.S. *A Review of Tropospheric Atmospheric Chemistry and Gas-Phase Chemical Mechanisms for Air Quality Modeling. Atmosphere.* **2012**, 3, 1-32.

Atmospheric lifetimes of neoteric short-lived HFCs against oxidation by the hydroxyl radical, and the resulting dry and wet deposition of trifluoroacetic acid in a WRF/Chem simulation

J. Kazil[1,2,*], S. McKeen[1,2], S.-W. Kim[1,2], R. Ahmadov[1,2], G. Grell[3],
R. K. Talukdar[1,2], A. R. Ravishankara[2]

[1] Cooperative Institute for Research in Environmental Sciences (CIRES), Boulder, CO, USA
[2] Chemical Sciences Division, NOAA Earth System Research Laboratory, Boulder, CO, USA
[3] Global Systems Division, NOAA Earth System Research Laboratory, Boulder, CO, USA
* Corresponding author: Jan.Kazil@noaa.gov

HFC-134a (1,1,1,2-tetrafluoroethane) is the prevalent refrigerant in automobile air conditioning units (MACs). With an atmospheric lifetime of ~14 years and a global warming potential (GWP) of 1370 on a 100-year time horizon, HFC-134a does not meet current and expected requirements for MAC refrigerants in many parts of the world. One of the simplest way to achieve lower GWP is to use chemicals with shorter atmospheric lifetimes. Two potential substitutes for HFC-134a have been put forth by industry: 2,3,3,3-tetrafluoropropene (TFP) and 1,2,3,3,3-pentafluoropropene (PFP). The WRF/Chem model was used to calculate atmospheric lifetimes of TFP and PFP against oxidation by the hydroxyl radical OH based on rate coefficients from laboratory experiments. The formation of trifluoroacetic acid (TFA) from TFP and PFP oxidation products was simulated in the model, and the dry and wet deposition of TFA over the contiguous USA during the May-September 2006 period that would result from replacing HFC-134a in MACs with a 1:1 molar ratio mixture of TFP and PFP was determined. We calculated the atmospheric lifetimes from this simulation to be ~5 and ~4 days for TFP and PFP, respectively. These lifetimes are approximately 50% shorter than previous estimates, which used a mean atmospheric OH concentration of 10^6 cm^{-3}. The shorter lifetimes obtained in the WRF/Chem simulation arise from a higher mean OH concentration of 1.5×10^6 cm^{-3}, and from spatial variability of OH concentrations, which are elevated in population centers, where TFP and PFP are preferentially emitted. Deposition of TFA was calculated to be highest in the eastern USA because of numerous large sources and high precipitation in the region. West of the Continental Divide, TFA deposition was significantly lower, and was attributable to emissions from California. Rainwater concentrations of TFA, averaged over the five-month simulation period remained, at all locations, below 0.1 mg L^{-1}; this threshold value is considered safe for the aquatic ecosystem. On shorter timescales, TFA rainwater concentrations can reach significantly higher values at locations with very low rainfall rates and low TFA deposition, mainly in California and Nevada. While the TFA rainwater concentrations expected from a replacement of HFC-134a with the shorter-lived TFP and PFP appear environmentally safe at most locations, TFA rainwater concentrations do not predict TFA concentrations in bodies of water, where accumulation may occur. The role of high TFA rainwater concentrations at locations with very low rainfall rates, and wash down of dry deposited TFA require further investigation.

Experimental and Theoretical Investigation of the OH-initiated Oxidation of Toluene

Renyi Zhang[1], Fei Xu[1], Jun Zhao[1], Hajime Terazono[2], Kentaro Misawa[2], Kazuhiko Shibuya[2]

[1] Department of Atmospheric Sciences and Department of Chemistry, Texas A&M University, College Station, TX 77843, USA

[2] Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, Tokyo 152-8551, Japan

Toluene is the most abundant aromatic hydrocarbon in the atmosphere and is emitted primarily from anthropogenic sources. Photochemical oxidation of toluene plays an important role in the formation of tropospheric ozone and secondary organic aerosol (SOA), which profoundly impacts air quality, human health, and climate, but its fundamental chemical mechanism remains largely uncertain. The oxidation of toluene is mainly initiated by the hydroxyl radical OH: the initial OH-toluene reaction results in minor H-abstraction (about 10%) and major OH addition (about 90%). The H-abstraction pathway leads to the formation of benzaldehyde, whose oxidative pathway is well established. The OH addition pathway results in the formation of methylhydroxycyclohexadienyl radicals (the OH-toluene adducts). Under atmospheric conditions, the OH-toluene adducts react with O_2 either by O_2 addition to form primary peroxy radicals, H-abstraction and subsequent O-bridge formation to aromatic oxide/oxepin, or H-abstraction to yield phenolic compounds. In this talk, we will present direct experimental product measurements and quantum chemical and kinetic calculations to elucidate the oxidation mechanism of the OH-initiated reaction with toluene, focusing the preferred pathways between the competing toluene-oxide/methyloxepin, peroxy radicals, and phenolic channels.

The atmospheric fate of methacrolein and a formation path for atmospheric aerosols

S. Jørgensen,[1*] H. C. Knap,[1] K. B. Ørnsø,[1] H. G. Kjaergaard,[1] J. D. Crounse,[2] P.O. Wennberg[2,3]

[1] Department of Chemistry, University of Copenhagen, 2100 Copenhagen, Denmark
[2] Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA 91125, USA
[3] Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA *
* Corresponding author: solvejg@chem.ku.dk

The oxidation of isoprene by the hydroxyl radical is known to produce aerosol in small yields (1). Aerosol production in laboratory chamber studies occurs in both high and low NOx environments. With low NOx, oxidation of isoprene is known to produce epoxides (IEPOX) in high yield (2). In chamber studies performed with high NOx, it has been shown that aerosol production follows the oxidation of a second generation oxidation product, MPAN, which is formed from methacrolein (MACR) (3).

Here we investigate the oxidation chemistry of MACR using quantum molecular calculations. We investigate both the reaction mechanism of hydrogen abstraction by OH (4) and the OH addition (5). The hydrogen abstraction reaction leads to either methyl-peroxyacetylnitrate (MPAN) or methyl peracrylicacid (MPAA) depending on whether the peroxyacetyl radical reacts with NO2 or HO2. High level quantum chemical calculations show, that the oxidation of MPAN leads to formation of hydroxymethyl-methyl-α-lactone (HMML) in high yield (4). HMML production follows a low potential energy path from both MPAN and MPAA following addition of OH (via elimination of the NO3 and OH from MPAN and MPAA, respectively). HMML is a plausible precursor for the formation of methyl glyceric acid (2-MG) and similar products, as lactones are known to undergo facile polymerization reactions (6). The addition of OH to MACR is expected to be followed by reaction with O2 leading to the formation of hydroxyl peroxy radical. This radical undergoes a fast (0.5±0.3 s-1 at T=296K) isomerization involving the 1,4-H-shift of the aldehydic hydrogen to the peroxide group (6) leading to hydroxyl hydroperoxy carbonyl radical, which decompose rapidly into hydroxyacetone and with a regeneration of OH.

References

(1) Kroll, J.H.; Ng, N.L.; Murphy, S.M.; Flagan, R.C.; Seinfeld, J.H. *Environ. Sci. Technol.* **2006**, 40,1869-1877.
(2) Paulot, F.; Crounse, J.D.; Kjaergaard, H.G.; Kurten, A.; St. Clair, J.M.; Seinfeld, J.H.; Wennberg, P. O. *Science* **2009**, 325, 730-733.
(3) Surratt, J.D.; Chan, A.W.H.; Eddingsaas, N.C.; Chan, M.; Loza, C.L.; Kwan, A.J.; Hersey, S.C.; Flagan, R.C.; Wennberg, P.O.; Seinfeld, J.H.. *Proc. Nat. Am. Soc.* **2010**, 107, 6640-6645.
(4) Kjaergaard, H.G.; Knap, H.C.; Ørnsø, K.B.; Jørgensen, S.; Crouse, J.D.; Paulot, F.; Wennberg. P.O. *Submitted to J. Phys. Chem A.*
(5) Crounse, J.D.; Knap, H.C.; Ørnsø, K.B.; Jørgensen, S.; Paulot, F.; Kjaergaard, H.G.; Wennberg, P.O. *Submitted to J. Phys. Chem. A*.
(6) L'abbe, G. Angew. *Chem. Int. Ed. Eng.* **1980**, 19, 276-289.

Uptake of glyoxal by organic and inorganic seed aerosols: Optical, physical and chemical properties of the product aerosols

M. Trainic,[1] A. A. Riziq,[1] A. Lavi,[1] J. M. Flores,[2,3] and Y. Rudich[1,*]

[1] Department of Environmental Sciences, Weizmann Institute, Rehovot 76100, Israel.
[2] Department of Particle Chemistry, Max Planck Institute for Chemistry, Mainz 55128, Germany
[3] University of Mainz, Institute for Atmospheric Physics, Mainz 55099, Germany

* Corresponding author: Yinon.rudich@weizmann.ac.il

Constraining the optical properties of secondary organic aerosol (SOA) is a major challenge since they often consist of a mixture of several components with various internal structures, including homogeneous mixtures and core/shell structures. The importance in understanding the optical properties of aerosols is their effect on the magnitude and uncertainty of Earth's total radiative forcing and climate change. SOA form by the condensation of less-volatile gaseous compounds onto pre-existing aerosols, and by heterogeneous and multi-phase reactions.

The heterogeneous reaction between glyoxal gas and three atmospheric aerosol types; ammonium sulfate (AS), glycine and glycine-AS 1:100 was studied. The optical extinction cross section at λ=355nm and mobility size increased following the reaction under a broad range of RH values (30-90%), indicating that the reaction is relevant for a wide range of atmospheric conditions.

We propose that at low RH values, below the deliquescence point, the reactions occur in interfacial monolayers of water, supporting previous findings about the importance of interfacial water in heterogeneous.

The reactions exhibit a trend of increasing growth in physical and optical cross sections with decreasing seed aerosol size, as well as a clear dependence on ambient RH values (Figure 1). For small particles with near-zero extinction efficiency (Q_{ext}) values, the reaction induces the greatest increase in optical extinction cross section (up to 2 orders of magnitude enhancement) due to a combined effect of changes in optical properties and in size, resulting in a change in the location on the Mie curve.

AMS analyses of the reactions show that the main reaction products are glyoxal oligomers, and a small contribution from the formation of various C-N compounds, identified as imidazoles.

Our results suggest that unlike previously postulated, the reactions at RH values below deliquescence occur on interfacial water layers and their optical enhancement is mainly due to enhanced scattering and geometric cross section growth.

This study contributes to the understanding of the effect of the reactions on the optical properties of the aerosols in the atmosphere by demonstrating that the heterogeneous reactions between abundant atmospheric components may alter the aerosols' optical, physical and chemical properties on short timescales (~ 1 hour) and may have substantial implications on the radiative effects of these aerosols.

O_3-initiated heterogeneous oxidation of linoleic acid and its dependences on ambient temperature and relative humidity

Guang Zeng[1,2], Yunhong Zhang[2*] and Yong Liu[1]*

[1]University of Colorado Denver, Denver, CO USA
[2]Beijing Institute of Technology, Beijing, China
*Corresponding author: yhz@bit.edu.cn; yong.liu@ucdenver.edu

Atmospheric aerosols are a complex mixture of inorganic and organic components and have been widely recognized as key elements in environmental issues ranging from air pollution, sky visibility, public health, to climate change. They often have a characteristic core-shell structure. Such a feature is inherent considering the properties of individual aerosol components, the aerosol emission sources, and their continuous aging while entrained in the air. As the organic coating is more likely to interact with reactive gaseous species than the inorganic core, the physiochemical properties of the organic surface determine, to a large extent, the environmental role of the aerosols. Despite recent extensive studies towards heterogeneous oxidation of unsaturated organics (mostly oleic acid) initiated by ozone[1-2], little is known about effects of ambient temperature and relative humidity on the chemical transformation of organic aerosols.

In this work, we used linoleic acid as a proxy for atmospheric unsaturated organics to investigate its heterogeneous oxidation by O_3 over a wide range of temperatures (257-313 K) and relative humidities (0-80% RH). Linoleic acid, which is found in lipids of cell membrane and plays important roles in various biologic processes, has been observed in atmospheric aerosols[3]. Our experiments were carried out using a flow reactor coupled to an attenuated total reflection infrared spectrometer (ATR-IR). Pseudo-first order rate constants and overall reactive uptake coefficients were acquired from absorbance changes in peaks located near 1743 cm^{-1}; 1710 cm^{-1}; 1172 cm^{-1} and 1110 cm^{-1}, which can be assigned to C=O in ester; C=O in acid; C-C and C-O stretching modes, respectively. Experimental results showed that heterogeneous loss of O_3 onto linoleic acid was highly efficient with an uptake probability close to 3×10^{-2} at 293K. It was found that the uptake coefficients increased with increasing temperature, and within the temperature range studied here the O_3 reactive uptake was enhanced by one order of magnitude. It was also noted such temperature enhancement effect on the reaction kinetics was much more effective at lower temperatures. For example, the Pseudo-first order rate constants increased nearly by 7-fold when temperature was changed from 257 K to 273 K. Such behavior can be explained by change in physical state of linoleic acid at lower temperatures which was confirmed by shifts of both CH_2 and C=O stretching modes. A decrease in absorbance ratio of (A_{1743}/A_{1710}) with decreasing temperature was also observed, an indicative of a smaller amount of α-acyloxyalkyl hydroperoxide-related products formed during oxidation of linoleic acid with O_3 at lower temperatures. In addition, RH study results showed that water vapor promoted heterogeneous reactive uptake of O_3 on linoleic acid surface. Furthermore, water uptake studies showed that O_3 initiated heterogeneous oxidation enhanced hydrophilicity of organic surface.

References

1. Carlton, A. G.; Wiedinmyer, C.; Kroll, J. H. A review of Secondary Organic Aerosol (SOA) formation from isoprene. *Atmospheric Chemistry and Physics* **2009**, 9 (14), 4987-5005.
2. Hildebrandt, L.; Donahue, N. M.; Pandis, S. N. High formation of secondary organic aerosol from the photo-oxidation of toluene. *Atmospheric Chemistry and Physics* **2009**, 9 (9), 2973-2986114.
3.Chebbi, A.; Carlier, A. Carboxylic acids in the troposphere, occurrence, sources, and sinks. *Atmospheric Environment* **1996**, 30 (24).

Heterogeneous Uptake of HO_2 Radicals onto Submicron Atmospheric Aerosols

P.S.J. Matthews,[1] I.J. George,[1] B. Brooks,[2,3] L.K. Whalley,[1,3]
M.T. Baeza Romero,[4] and D.E. Heard[1,3,*]

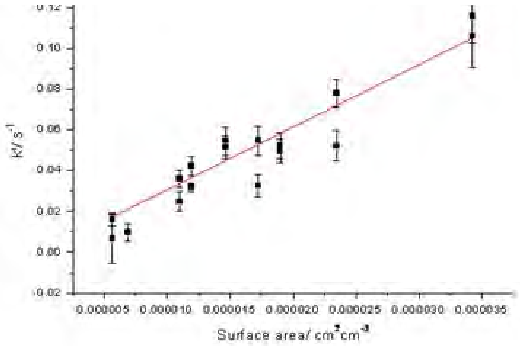
[1]School of Chemistry, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK
[2]School of Earth and Environment, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK
[3]National Centre for Atmospheric Chemistry, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK
[4]Escuela de Ingenieria Industrial de Toledo, Universidad de Castilla la Mancha, Toledo, 45071, Spain
* Corresponding author: d.e.heard@leeds.ac.uk

Field measurement studies have reported significantly lower HO_2 radical concentrations than calculated by constrained box models using detailed chemical mechanisms. Although in some cases for the marine boundary layer (MBL) part of the discrepancy has now been attributed to the influence of halogen chemistry (1,2), uptake of HO_2 by aerosols is postulated as a loss mechanism, for example in the MBL (2) the Arctic tropopshere (3) and the upper troposphere (4). However, there have been very few laboratory studies on HO_2 uptake by aerosols and the rates and mechanism of the HO_2 loss by aerosols are still uncertain.

The HO_2 uptake coefficients for a range of inorganic and organic aerosols have been measured at room temperature and atmospheric pressure using an aerosol flow tube combined to a Fluorescence Assay by Gas Expansion (FAGE) detector. The sensitive FAGE method enables low concentrations (10^8-10^9 molecule cm^{-3}) of HO_2 to be injected into the aerosol flow tube using a moveable injector, and position dependent decay profiles of HO_2 are recorded as a function of aerosol surface area. The aerosols were generated using an atomiser or by using homogeneous nucleation, and the particle size and number distributions were measured with a Scanning Mobility Particle Sizer.

The HO_2 uptake coefficient (γ) was measured for dry inorganic aerosols (γ= 0.000-0.001), wet inorganic aerosols (γ= 0.002-0.005), wet copper doped ammonium sulfate aerosols (γ= 0.28, Figure 1) and ammonium sulfate aerosols doped with different molar amounts of iron (γ=0.003-0.06). The pH dependence of the HO_2 uptake coefficient was also investigated, however, no dependence was observed. The HO_2 uptake coefficients onto a range of both wet and dry organic aerosols were found to be small (γ<0.008) with the exception of humic acid aerosols which had a larger uptake coefficient that was also dependent on relative humidity (γ=0.008-0.13). However, humic acid was found to contain metals, which may explain the higher uptake coefficient. HO_2 uptake coefficients are currently being measured at low temperature for a range of aerosols.

Figure 1. HO_2 uptake onto Cu doped $(NH_4)_2SO_4$ aerosols at RH = 53%, giving $\gamma = 0.28 \pm 0.05$.



This work was supported by the National Environment Research Council under grant number NE/F020651/1. PSJM is grateful to NERC for a research studentship.

References

(1) Sommariva, R. *et al. Atmos. Chem. Phys.* **2006**, 6, 1135-1153.
(2) Whalley, L.K. *et al. Atmos. Chem. Phys.* **2010**, 10, 1555-1576.
(3) Mao, J. *et al. Atmos. Chem. Phys.* **2010**, 10, 5823-5838.
(4) Jaegle, L. *et al. J. Geophys. Atm.* **2000**, 105, 3877-3892.

Physical, Chemical, and Hygroscopic Properties of Submicrometer Particles Studied by X-ray Spectro-Microscopy

Alexei V. Tivanski,[1,*]

[1] University of Iowa, Iowa City, IA, USA
* Corresponding author: alexei-tivanski@uiowa.edu

Atmospheric aerosols are a complex micro-structured mixture of inorganic and organic components, where organics can represent more than 50% of the aerosol mass depending on location. Understanding and predicting the climate effects due to atmospheric aerosols requires quantitative knowledge of their hygroscopic and chemical properties. The ability of aerosols to absorb water influences their optical and cloud forming properties, ice nuclei formation and transformation, atmospheric lifetime, and chemical reactivity. The presence of organic carbon in aerosols has a complex effect on their physical-chemical and reactive properties that is poorly understood. In particular, there is a lack of robust quantitative measurements on how properties of organic components (such as particle size, morphology, chemical composition, concentration and type of mixing) influence the rate and amount of water uptake on aerosols.

Here we present a unique application of single particle Scanning Transmission X-ray Microscopy (STXM) and Atomic Force Microscopy (AFM) for quantitative analysis of density, elemental and chemical compositions, type of mixing, and hygroscopic properties of individual submicron particles. The approach utilizes AFM for direct determination of three-dimensional shape of substrate-deposited particles followed by STXM spectro-microscopy analysis performed during exposure to water vapor at different relative humidity (RH). The hygroscopic properties of atmospherically-relevant NaCl, NaBr, NaI, $NaNO_3$, malonic acid and glutaric acid, as well as several mixed organic and inorganic submicron particles were measured to evaluate the utility of the approach. A model was developed that allows quantitative determination of the mass of liquid water and water-to-solute ratio(WSR) in a submicron aerosol. The results for the deliquescence and efflorescence phase transitions and quantitative measurements of water-to-solute ratios are found in excellent agreement with available literature data.[1] Near edge X-ray absorption spectroscopy (NEXAFS) was utilized to determine and quantify efficient keto-enol tautomerization of malonic acid, with the enol form dominating at higher RH. The keto-enol equilibrium constants were calculated using the NEXAFS spectra as a function of RH and were found to be up to four orders of magnitude higher than the solution equilibrium constants. Our results suggest that in deliquesced particles, carboxylic acids may exist in their enol forms that need to be explicitly considered in atmospheric aerosol chemistry.[2]

References

(1) S. Ghorai, A.V. Tivanski *Anal. Chem* **2010**, 82, 9289-9298.
(2) S. Ghorai et al *J. Phys. Chem. A* **2011**, 115, 4373-4380.

OH-initiated heterogeneous aging of highly oxidized organic aerosol

Sean H. Kessler[1], Theodora Nah[2,3], Kelly E. Daumit[4], Jared D. Smith[2], Stephen R. Leone[3], Charles E. Kolb[5], Douglas R. Worsnop[5], Kevin R. Wilson[2], Jesse H. Kroll[1,4*]
[1] Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge MA 02139
[2]Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley CA 94720
[3]Department of Chemistry, University of California, Berkeley, CA 94720
[4] Department of Civil & Environmental Engineering, Massachusetts Institute of Technology, Cambridge MA 02139
[5]Center for Aerosol and Cloud Chemistry, Aerodyne Research Inc., Billerica MA 01821

[*]Corresponding author: jhkroll@mit.edu

The oxidative evolution ("aging") of organic species in the atmosphere is thought to have a major influence on the composition and properties of organic particulate matter, but remains poorly understood, particularly for the most oxidized fraction of the aerosol. Here we measure the kinetics and products of the heterogeneous oxidation of highly oxidized organic aerosol, with an aim of better constraining atmospheric aging processes of oxidized compounds, which are found primarily in the condensed phase. Submicron particles composed of model oxidized organics—1,2,3,4-butanetetracarboxylic acid ($C_8H_{10}O_8$), citric acid ($C_6H_8O_7$), tartaric acid ($C_4H_6O_6$), and Suwannee River fulvic acid—were oxidized by gas-phase OH in a flow reactor, and the masses and elemental composition of the particles were monitored as a function of OH exposure. In contrast to our previous studies of less-oxidized model systems (squalane, erythritol, and levoglucosan), particle mass did not decrease significantly with heterogeneous oxidation. Carbon content of the aerosol always decreased somewhat, but this mass loss was approximately balanced by an increase in oxygen content. The estimated reactive uptake coefficients of the reactions range from 0.37 to 0.51 and indicate that such transformations occur at rates corresponding to 1-2 weeks in the atmosphere, suggesting their importance in describing the atmospheric lifecycle of organic particulate matter.

Interaction of HONO with mineral oxides: uptake and products

Manolis Romanias, Atallah El Zein, and Yuri Bedjanian*

Institut de Combustion, Aérothermique, Réactivité et Environnement (ICARE), CNRS, Orléans, France
* Corresponding author: yuri.bedjanian@cnrs-orleans.fr

HONO is an important atmospheric species representing a significant daytime source (via photolysis) of OH radical, the major atmospheric oxidant. The mechanisms of HONO formation in the atmosphere are still not completely understood. One current issue in the chemistry of HONO is that the models fail to reproduce unexpectedly high daytime concentrations of HONO observed in field studies, indicating the existence of new, yet unknown, daytime sources of HONO. Heterogeneous processes, including those on humid surfaces, being thought to be the major source of HONO in the atmosphere, have been intensively studied in the laboratory and several mechanisms of HONO formation on aerosol and ground surface have been proposed. Conversely, the atmospheric aerosol can also act as a sink for gaseous HONO, probably, hardly competitive with HONO photolysis during the day, but potentially important during nighttime. The information on the nature, rate and products of HONO interaction with solid surfaces of atmospheric interest is very scarce and seems to be limited to a few studies carried out with ice and soot surface.

The present work reports the results of an experimental study of the kinetics and products of the heterogeneous reaction of HONO with different constituents of mineral aerosol (TiO_2, Al_2O_3, Fe_2O_3) and Arisona Test Dust (ATD). The interaction of HONO with solid films of the mineral oxides was studied for the first time under dark and UV irradiation conditions using a low pressure flow reactor (1 – 10 Torr) combined with a modulated molecular beam mass spectrometer for monitoring of the gaseous species involved. The reactive uptake of HONO was studied as a function of HONO concentration, relative humidity (RH = 3×10^{-4} – 60 %), temperature (T = 275 – 320 K) and irradiance intensity ($J_{NO2} = 0.002 – 0.012\ s^{-1}$). A deactivation of mineral oxide surface upon exposure to HONO was observed. The measured initial uptake coefficients of HONO were found to be independent of the HONO concentration and temperature. The effect of UV irradiation on the reactivity of HONO (increase of uptake) was observed for TiO_2 and Al_2O_3 surfaces only and was negligible for ATD and Fe_2O_3. The relative humidity (RH) was found to have a strong impact on the uptake coefficient: $\gamma_0 \sim (RH)^{-\alpha}$, with $\alpha \approx 0.65$, for all samples under dark conditions and $\alpha \approx 0.3$ and 0.45 on irradiated TiO_2 and Al_2O_3 films, respectively.

NO_2 and NO were observed as products of the HONO reaction with all mineral oxides studied with the sum of their yields corresponding to nearly 100% of the nitrogen mass balance. The yields of NO and NO_2 were found to be around 40 and 60 %, respectively, independent of relative humidity, temperature, concentration of HONO and irradiance intensity on all surfaces except TiO_2 under irradiation where similar (~ 50%) yields of NO and NO_2 were observed.

Mechanism for nighttime loss and daytime production of HONO at ground surfaces: Reactive uptake and displacement

Trevor C. VandenBoer,[1] Cora J. Young,[2,3*] Ranajit K. Talukdar[2,3], Steven S. Brown[3], James M. Roberts[3], Jennifer G. Murphy[1]

[1] Department of Chemistry, University of Toronto, Toronto, ON, Canada
[2] Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO, USA
[3] Chemical Sciences Division, National Oceanic and Atmospheric Administration (NOAA), Boulder, CO, USA
* Corresponding author: cora.young@noaa.gov

Nitrous acid (HONO) is an important source of hydroxyl radicals in the troposphere, particularly in early morning. Formation of HONO from the precursor NO_2 is known to occur through heterogeneous mechanisms, with accumulation overnight, followed by photolysis in the morning. Observations have been made of HONO during the day that cannot be fully explained by current formation mechanisms. Understanding these mechanisms is critical to determining the full role of HONO as a radical source.

Recent field observations of nitrite in particles suggest that partitioning and/or reactive uptake may also play a role in the atmospheric chemistry of HONO. Models using currently understood mechanisms require additional unknown night-time sinks and day time sources to reconcile measured levels of HONO. These sinks and sources remain significant points of uncertainty in understanding HONO atmospheric chemistry. In this study we explore the reactive uptake of HONO on soil-salt surrogates and real soil extracts as a function of relative humidity at atmospheric temperature and pressure. Measurements were made using a negative-ion proton-transfer mass spectrometer and cavity ring-down spectrometer to track acids and nitrogen oxides, respectively. Uptake of HONO onto salts could be reversed by exposure to the strong acids HCl and HNO_3, which may act as a realistic daytime source of HONO.

Kinetics and Mechanism Investigation for Carboxylic acids (R–C(O)OH, R: –CH_2CH_3, –$CH_2CH_2CH_3$) Uptakes on Pure and HNO_3-Doped Ice Surfaces under UT/LS Temperature Conditions.

Manolis N. Romanias,[1] Vassileios C. Papadimitriou,[1] and Panos Papagiannakopoulos[1,*]

[1] University of Crete, Department of Chemistry, Heraklion, Greece
* Corresponding author: panosp@chemistry.uoc.gr

In the present work, the heterogeneous interaction of $CH_3CH_2C(O)OH$ and $CH_3CH_2CH_2C(O)OH$ with pure and HNO_3-doped ice surfaces (1.96 and 7.69 wt % H_2O/HNO_3) under UT/LS temperature conditions was studied at the low pressure regime (~2 mTorr). Experiments were carried out in a Knudsen continuous-flow reactor coupled with quadrupole mass spectrometry (Kn–QMS). Pure and HNO_3–doped ice surfaces of ~5 – 20 μm thickness were developed at T = 206 K, by single capillary controlled flow of H_2O vapors (pure ice films) or by H_2O vapors and HNO_3/He mixture co-admission (HNO_3–doped ice films) via separate inlets in the reactor, followed by their deposition on the cold copper surface at the bottom of the Knudsen cell. The initial uptake coefficients of the title carboxylic acids were measured as a function of temperature (195-212 K), for the three different types of the ice films, varying the R-C(O)OH concentration in the range $(0.18 – 17.83) \times 10^{11}$ molecule cm^{-3}. Initial uptake coefficients, γ_0, of both carboxylic acids showed inverse temperature dependence, while the γ_0 values that were measured for boutanoic acid were systematically higher compared to those of propanoic acid. The latter result is consistent with what was observed for the carboxylic acids of smaller straight-carbon chain (X–C(O)OH, X: –H, –CH_3), resulting, eventually, in a γ_0 value increase of a factor of 10, from HC(O)OH to $CH_3CH_2CH_2C(O)OH$.[1,2] HNO_3 doping of the ice surfaces had a negligible effect on γ_0 values. However, noticeable differences of R–C(O)OH surface coverage on, and desorption from the ice surface were observed in case by case of the series of carboxylic acids. This can be attributed to an increase of ice surface reactivity due to in-bulk phenomena, such as diffusion or/and dissolution, and the deterioration of ice-structure smoothness that they are explicitly discussed. Finally the lifetime of propanoic and boutanoic acid (τ_{het}) at dense cirrus clouds particles ($\sim 2\times10^{-4}$ cm^2 cm^{-3}) was estimated and the significance of the heterogeneous chemistry as a potential sink is compared to the gas phase chemistry.

References

(1) Romanias, M.N.; Zogka, A.G.; Stefanopoulos, V.G.; Papadimitiou, V.C.; Papagiannakopoulos, P. *Chemphyschem.* **2010**, 18, 4042 – 4052.
(2) Romanias, M.N.; Zogka, A.G.; Papadimitiou, V.C.; Papagiannakopoulos, P. *J. Phys. Chem. A* **2012**, DOI: 10.1021/jp205196t.

Effect of Aerosol Surface Nature on Phenomenon of Radicals Multiplication during Heterogeneous Interaction of Peroxy Radicals with Organic Compound

I.A.Vardanyan*,[1] A.M. Arustamyan,[1] L.A. Manucharova,[1] S.V. Tsarukyan[1]
[1] A.B. Nalbandyan Institute of Chemical Physics, National Academy of Sciences, Yerevan, Armenia
*Corresponding author: ivardan@ichph.sci.am

Interest to study of heterogeneous radical reactions is stipulated by several reasons. At first, similar stages take place at gas phase oxidation of organic compounds (RH). Second, at the presence of aerosols in an atmosphere they can influence on a rate of the photochemical degradation of organic compounds and, thus, on the composition of an atmosphere.

In this work the results of the investigation of the reaction between radicals and organic compound (CH_4, CH_3CHO) at room temperature dependent on surface nature (TiO_2, NH_4NO_3, NaCl and KCl) are reported. These compounds present in the form of aerosols in atmosphere. Experiments were carried out with the help of the method designed by us using ESR spectrometer and radicals freezing. The heterogeneous radical stages in flow in a capillary glass reactor (l = 2 cm, d = 0.14 cm) at low pressures (10^{-2} Torr) were studied. These experimental conditions allow to reduce the contribution of the homogeneous interaction of radicals to a minimum. The surface of a reactor was treated by solutions of indicated compounds, accordingly.

Peculiarities of the interaction of CH_3O_2 radicals with organic compound dependent on the surface nature were analyzed generally by the example of CH_4. Comparison of the regularities of the change of quantity of radicals (ΔRO_2) from a quantity of methane has shown the sharp difference both in the quantitative, and in qualitative aspect. In case of NaCl and KCl salts only the diminution of a quantity of radicals was observed, being on NaCl much more. On TiO_2 and NH_4NO_3 alongside with the more significant consumption of radicals at small amounts of methane, the multiplication of radicals with the further rise of CH_4 amount has been observed, i.e. the amount of detected radicals exceeds their initial amount (on 18 and 47 %, correspondingly). The consumption proceeds more intensively on NH_4NO_3 surface. Apparently the radicals multiplication is observed only in case of an oxygen-containing surface.

Radicals consumption is attributed to the stage $CH_3O_2 + CH_4 \rightarrow CH_3OOH + CH_3$ (1) while radicals multiplication can be attributed to the additional consumption of organic compound by the chain degenerate branching mechanism because of heterogeneous radical decay of CH_3OOH. This fact allows assuming the participation of the lattice oxygen in the interaction peroxy radicals with RH.

The model of chain consumption of organic compound, initiated by a stage (1) has been offered and analyzed in approximation both Langmuir-Hinshelwood and Readyl-Ealy at the presence of oxygen traces to the qualitative explanation of the experimentally observed phenomenon. The application limits of these approximations were established dependent on adsorption capacity of compounds and a rate constant of the stage (1).

From the obtained data follows, that at the presence of aerosols the contribution of heterogeneous reaction of radicals with various organic compounds can influence on the processes proceeding in atmosphere. Detailed elaboration of the concrete mechanism of interaction with an active site of a surface is a subject of the further investigations.

Flame synthesis of iron oxide nanoparticles

Marina Poliak[1], Amir Hevroni[1] ,Igor Rahinov[2], Vladimir Tsionsky[1], and Sergey Cheskis,*[1]

[1] Tel Aviv University, Tel Aviv, Israel
[2] Open University of Israel, Raanana, Israel
* Corresponding author: cheskis@post.tau.ac.il

The description of the detailed kinetics of the nanoparticle formation during combustion synthesis is an open and widely-debated topic, since combustion synthesis is of considerable interest both in fundamental and applied research. The main challenge in such kind of studies is the heterogeneity of the system, which demands employing diagnostics integrating state-of-the art methods from several fields.

In this work we studied the kinetics and the mechanism of the formation of iron oxide nanoparticles in a low pressure hydrocarbon flame doped with iron pentacarbonyl. The newly-built apparatus allowing to combine several methods for characterization of both gas phase intermediate molecules and solid state nanoparticles was used for this purpose. For measurement of spatial profiles of nanoparicle concentration and their sizes a method integrating molecular beam particle mass spectrometer (PMS) and quartz crystal microbalance (QCM) was employed (1). PMS allows measurements size distribution of charged nanoparticles and QCM provides information about total nanoparticle mass concentration distribution in flame.

For diagnostics of molecular species in flame various spectroscopic methods were employed. Cavity Ring Down spectroscopy (CRDS) and Laser Induced fluorescence were used for measurement of temperature distribution and concentration profiles of Fe atoms. CRDS was used also for additional characterization of nanoparticles formed in flames. Results of the experiments and their comparison with current models of nanoparticle formation are discussed.

References

(1) Hevrony, A.; Golan, H.; Fialkov, A.; Rahinov, I.; Tsionsky, V.; Markovich, G.; Cheskis, S. *Measur. Sci. Tech.* **2011,** 22, 115102.

Some features of realization of three-stage mechanism of ionic recombination

V.M. Azriel*, L.Yu. Rusin

Institute of Energy Problems of Chemical Physics, Moscow, Russia
* Corresponding author: Azriel_Vladimir@mail.ru

One of the basic considered in the kinetic literature mechanisms of recombination of ionic pair A^+ and B^- with participation of atom-acceptor of energy C can be represented by the following scheme including three consecutive two-body collisions:

$$A^+(B^-) + C \leftrightarrow CA^{+}{*}(CB^{-}{*}) \qquad (1)$$
$$CA^{+}{*}(CB^{-}{*}) + C \rightarrow CA^+(CB^-) + C \qquad (2)$$
$$CA^+(CB^-) + B^-(A^+) \rightarrow AB + C \qquad (3)$$

In this scheme at a stage (1) there is a formation of intermediate weakly bounded complex of one of ions with atom C. At the second stage this complex is stabilized by collision with the second atom-acceptor of energy and further at a stage (3) as a result of interaction of an ionic complex with the second ion participating in recombination the molecule AB as a final product of recombination is formed. However, formed at a stage (2) stabilized ionic complex can collide not with the second ion, but with possessing sufficient energy another atom C that owing to low bond energy inside the complex can lead to its dissociation on constituent components:

$$CA^+(CB^-) + C \rightarrow C + A^+(B^-) + C \qquad (4)$$

The competition of channels (3) and (4) is investigated by a method of classical trajectories on a example of process of recombination in system $Cs^+ + Br^- + Xe$ for a case when at a stage (1) ionic complex $XeCs^+$ is formed in a range of collision energies from 0 to 10,0 eV. Excitation functions of processes (3) and (4) are shown on figure 1 from which it follows that at collision energies above 1,0 eV the probability of decomposition of ionic complex $XeCs^+$ on constituent components considerably exceeds probability of formation of molecule CsBr in channel (3).

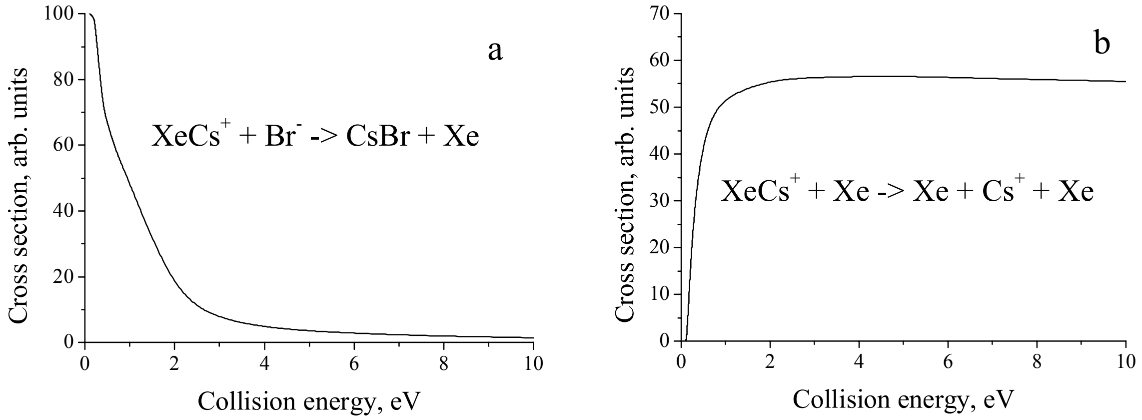


Fig.1. Excitation functions of the channels of formation of molecules CsBr (a) and decomposition of an ionic complex (b) in a range of collision energies from 0 to 10,0 eV.

Low Temperature Measurements of Electron Attachment to $POCl_3$

G.Saidani[1*], S. Carles[1], C.Berteloite[1], J.L. LeGarrec[1], J.B.A. Mitchell[1], A.A. Viggiano[2]

[1] Institut de Physique de Rennes UMR 6251 CNRS
[2] Air Force Research Laboratory, Space Vehicles Directorate, Hanscom Air Force Base, Bedford, Massachusetts 01731-3010, USA.
* Corresponding author: saidanighassen@gmail.com

The solution phase chemistry of phosphorous trichloride ($POCl_3$) is well characterized as this molecule is used in a number of industrial processes including the synthesis of important organophorous compounds [1], such as flame retardants, plasticizers, insecticides and fuel additives. However, the gas phase chemistry of $POCl_3$, including the ion-molecule and electron-molecule reactions, has not been well studied especially at low temperatures despite the fact that the pure substance have relatively high vapor pressure. In the present work, we have investigated the reactivity of $POCl_3$ with thermal electrons and have measured their attachment rate constants at different temperatures in a low density plasma ($\sim 10^9$ cm^{-3}) using the CRESU technique. This reaction displays at low temperature (39K-170K), a high rate constant of $\sim 10^{-7}$ cm^3 molecule^{-1}s^{-1} and is a relatively temperature dependent in our temperature range [2]. Electron attachment to $POCl_3$ is a rich process in which a non-dissociative channel ($POCl_3^-$) competes with a dissociative one ($POCl_2^-$) [3]. We have shown that the main product at low temperature ($\leq$170K) is $POCl_3^-$, which is the non dissociative channel, where the reaction is governed by termolecular collisions. At higher temperature it is rather the dissociative one which prevails confirming others studies at higher temperatures [3-6].

References

1. Sanderson, R.T., Simple Inorganic Substances: A New Approach (Drieger, Malabar, FL, 1989), pp. 336–343.
2. Shuman, N.S., et al., *Electron attachment to $POCl_3$. II. Dependence of the attachment rate coefficients on gas and electron temperature.* International Journal of Mass Spectrometry. **306** p. 123-128.
3. Shuman, N.S., et al., *Electron attachment to $POCl_3$. III. Measurement and kinetic modeling of branching fractions.* The Journal of Chemical Physics. **134**(9): p. 094310-10.
4. Miller, T.M., et al., *Electron attachment to PCl_3 and $POCl_3$, 296--552 K.* The Journal of Chemical Physics, 1998. **109**(2): p. 578-584.
5. Van Doren, J.M., et al., *Electron attachment to $POCl_3$: Measurement and theoretical analysis of rate constants and branching ratios as a function of gas pressure and temperature, electron temperature, and electron energy.* The Journal of Chemical Physics, 2006. **124**(12): p. 124322-9.
6. Williamson, D.H., et al., *Effect of pressure and temperature on the competition between nondissociative and dissociative electron attachment to $POCl_3$.* The Journal of Chemical Physics, 2000. **113**(24): p. 11035-11043.