

## NASA GRANT NAGW-4209

FINAL TECHNICAL REPORT FOR BUDGET PERIOD  
JUNE 1, 1994 - MAY 30, 1995

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The 1994 BOC Priestley Conference was held at Bucknell University in Lewisburg, Pennsylvania, from June 24 through June 27, 1994. This conference, managed by the American Chemical Society (ACS), was a joint celebration with the Royal Society of Chemistry (RSC) commemorating Joseph Priestley's arrival in the U.S. and his discovery of oxygen. There were 120 attendees.

The basic theme of the conference was "Oxidants and Oxidation in the Earth's Atmosphere," with a keynote lecture on the history of ozone. (A copy of the final program is attached.) A distinguished group of U.S. and international atmospheric chemists addressed the issues dominating current research and policy agendas. Topics crucial to the atmospheric chemistry of global change and local and regional air pollution were discussed.

The program for the conference included four technical sessions on the following topics:

1. Oxidative Fate of Atmospheric Pollutants
2. Photochemical Smog and Ozone
3. Stratospheric Ozone
4. Global Tropospheric Ozone

The format of the conference consisted of three morning and one afternoon session of three to five forty-minute presentations. Each presentation was followed by twenty minutes of discussion and debate. Senior atmospheric chemists chaired each session and lead the discussions. Twenty posters also were presented during the organized poster session.

(NASA-CR-197945) OXIDANTS AND  
OXIDATION IN THE EARTH'S ATMOSPHERE  
Final Technical Report, 1 Jun. 1994  
- 30 May 1995 (American Chemical  
Society) 17 p

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Bucknell University  
Lewisburg, Pennsylvania  
USA

June 24-27, 1994

## 7th BOC Priestley Conference

### Technical Theme:

The Chemistry of the  
Atmosphere---Oxidants  
and Oxidation in the  
Earth's Atmosphere

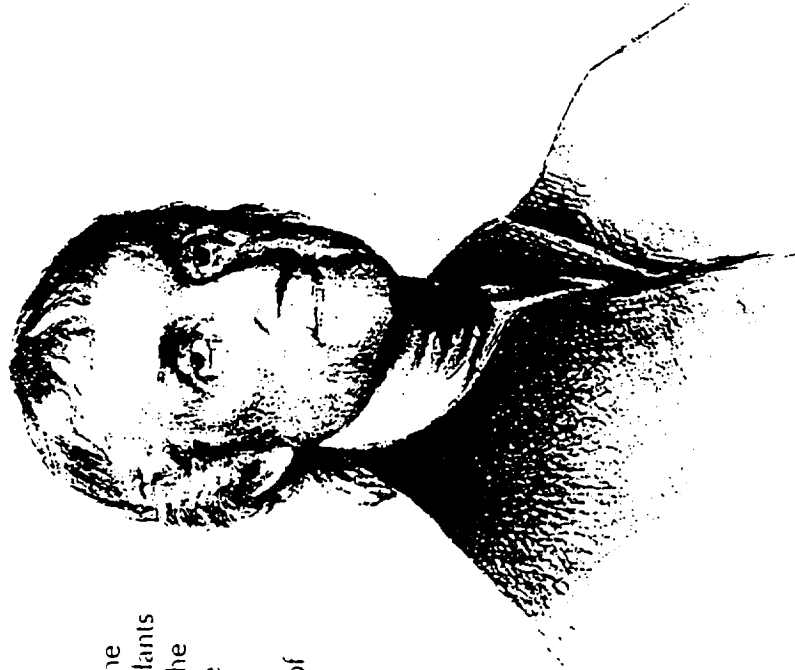
### Historical Theme:

The Early History of  
Ozone

### Organized By:

The Royal Society  
of Chemistry  
with the  
cooperation of  
the American  
Chemical  
Society

### Program



## SCIENTIFIC PROGRAM

### FRIDAY 24 JUNE

20.00 Introductions

*The Forum*

J. W. Barrett, Chairman, BOC Organizing Committee, UK

C. W. Rees, President, Royal Society of Chemistry, UK

N. D. Heindel, President, American Chemical Society, USA

G. A. Sojka, President, Bucknell University, USA

20.10 Introduction of Plenary Historical Lecture

J. W. Barrett, Chairman, BOC Organizing Committee, UK

Lecture: C. A. Russell, The Open University, UK

20.30 Introduction of Keynote Lecture

A. R. Bandy, Drexel University, USA

Ozone: a Minor Oxygen Allotrope, a Major Factor in  
Atmospheric Chemistry

P. J. Crutzen, Max-Planck-Institute for Chemistry, Germany

21.30 RECEPTION

*Terrace Room*

### SATURDAY 25 JUNE

TECHNICAL SESSION I:

OXIDATIVE FATE OF ATMOSPHERIC POLLUTANTS

*The Forum*

Chairman: R. A. Cox, Natural Environmental Research  
Council, Swindon, UK

08.30 1.1

Bromine Sensitized Decomposition of Ozone

R. A. Cox, Natural Environmental Research Council,  
UK

09.15 1.2

Atmospheric Models of Chemical Fate

J. M. Rodriguez, Atmospheric & Environmental  
Research, USA

10.00 COFFEE

10.30	1.3	Heterogeneous Degradation of Oxygenated Intermediates E. O. Edney, U.S. EPA, Office of Research & Development, USA	
11.15	1.4	Initiation of Chemical Removal Processes R. Atkinson, University of California, Riverside, USA	
12.00	LUNCH		<i>Cafeteria</i>
<b>TECHNICAL SESSION II: PHOTOCHEMICAL SMOG AND OZONE</b>			
Chairman: K. L. Demerjian, Atmospheric Sciences Research Center, USA			
13.15	2.1	Ozone Formation and Photochemical Smog in Urban and Regional Atmospheres J. H. Seinfeld, California Institute of Technology, USA	<i>The Forum</i>
14.00	2.2	Ozone Formation in Anthropogenically Perturbed Regions and Global Change W. L. Chameides, Georgia Institute of Technology, USA	
14.45	2.3	Regulatory Aspects of Tropospheric Ozone J. D. Bachmann, U.S. EPA, Office of Air Quality Planning & Standards, USA	
15.30	2.4	Fuels, Vehicles and Their Impact on Urban Ozone A. M. Dunker, General Motors Research & Development Center, USA	
16.15		TEA AND DEPARTURE FOR SUSQUEHANNA UNIVERSITY (Buses depart from Lagone Center)	
20.00	BARBECUE		<i>Swartz Hall Field</i>

## SUNDAY 26 JUNE

08.30	Poster Session		<i>The Cave</i>
<b>TECHNICAL SESSION III: STRATOSPHERIC OZONE</b>			
Chairman: A. R. Ravishankara, NOAA, USA			
10.30	3.1	Stratospheric Ozone and Humankind: What We've Learned and What We Still Need To Know D. L. Albritton, Aeronomy Laboratory, NOAA, USA	<i>The Forum</i>
11.15	3.2	Chemical Mechanism of Atmospheric Ozone Depletion M. J. Molina, Massachusetts Institute of Technology, USA	
12.00	LUNCH		<i>Cafeteria</i>
13.15	3.3	Free Radical Catalysis: What do <i>In Situ</i> Observations Tell Us? J. G. Anderson, Harvard University, USA	
14.00	3.4	Photochemistry and Heterogeneous Chemistry in the Stratosphere S. C. Wofsy, Harvard University, USA	
14.45	3.5	Three Dimensional Modeling of Stratospheric Ozone J. Pyle, Cambridge University, UK	
15.30		TEA AND DEPARTURE FOR NORTHUMBERLAND (Buses depart from Lagone Center)	
20.00	PRIESTLEY DINNER		<i>Terrace Room</i>

## MONDAY 27 JUNE

### TECHNICAL SESSION IV: GLOBAL TROPOSPHERIC OZONE

*The Forum*

Chairman: S. A. Penkett, University of East Anglia, Norwich, UK

- 08.30 4.1 Overview of Tropospheric Ozone Distribution and Global Implications  
J. Fishman, NASA, Langley Research Center, USA
- 09.15 4.2 Ozone Changes in the Future - Key Processes and Prediction of Trends  
A. M. Thompson, NASA/Goddard Space Flight Center, USA

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10.00 COFFEE

- 10.30 4.3 Impact of Commercial Aircraft on Tropospheric Ozone  
D. H. Ehhalt, Institut für Atmosphärische Chemie, Jülich, Germany

- 11.15 CONCLUDING KEYNOTE LECTURE  
The Chemistry of Atmospheric Oxidants: Where Do We Go From Here?  
C. E. Kolb, President, Aerodyne Research, USA

12.15 Concluding Remarks

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12.30 LUNCH AND CLOSURE OF CONFERENCE *Cafeteria*

## HISTORICAL PROGRAM

EARLY HISTORY OF OZONE

Room 301-Gallery Theatre

### SUNDAY 26 JUNE

- Introduction: C. A. Russell, The Open University, UK
- 08.30 11.1 The Discovery of Ozone  
A. Roche, Case Western Reserve University, USA

- 09.15 11.2 Analytical Work on Ozone  
D. Thorburn Burns, Queen's University of Belfast, UK

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10.00 COFFEE

- 10.30 11.3 Ozonisers of Old and New  
W. H. Brock, University of Leicester, UK

- 11.15 11.4 Ozonolysis and Organic Structures and Ozone Structures  
P. J. Morris, Science Museum/Open University, UK

- 12.00 11.5 Ozone and Its Structure  
N. G. Coley, Open University, UK

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12.45 LUNCH

Introduction: A. Roche, Case Western Reserve University, USA

- 14.00 11.6 Ozone and the Environment  
S. Wilnot, Open University, UK

- 14.45 11.7 Ozone in Industry and Commerce  
W. A. Campbell, University of Newcastle upon Tyne/Open University, UK

- 15.30 TEA AND DEPARTURE FOR NORTHUMBRLAND  
(Buses depart from Lagone Center)

20.00 PRIESTLEY DINNER

*Terrace Room*

The social program is as follows:

**FRIDAY**

21.30 Reception following Keynote Lecture      *Terrace Room*  
(Gratis for all participants)

**SATURDAY**

16.30 RECEPTION (Gratis for all participants)  
at Susquehanna University Art Gallery. Associated with this  
reception will be a special exhibition celebrating Priestley's  
encounter with America, entitled "Joseph Priestley's Ameri-  
can Legacy". Buses begin departing from Lagone Center at  
16.15.

20.00 Barbecue (Gratis for all participants)      *Swartz Hall Field*

**SUNDAY**

15.30 Wine and Cheese Party (Gratis for all participants)  
at the Priestley House in Northumberland. Compliments of  
the Pennsylvania Historical and Museum Commission.  
Buses begin departing from Lagone Center at 15.30.

20.00 Priestley Dinner (Ticketed)      *Terrace Room*

A toast to the immortal memory of Joseph Priestley  
will be proposed by Lord Dainton. Recipients of the  
American Chemical Society's Priestley Medal are being  
invited.

# ABSTRACTS

TERMINATION OF CFC AND HFC PHOTO-OXIDATION PROCESSES. REACTION KINETICS OF  $\text{FC(O)O}$ . I. S. Dibble and J. S. Francisco, Department of Chemistry, Wayne State University, Detroit, MI 48202, M. Matti Maricq and J. J. Szentle, Research Laboratory, Ford Motor Company, P.O. Box 2053, Dearborn, MI 48121.

The kinetics of reactions of  $\text{FC(O)O}$  with  $\text{O}_3$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{HO}_2$  are studied using laser photolysis and UV-visible absorption spectroscopy for  $233 \text{ K} < T < 323 \text{ K}$ .  $\text{FC(O)O}$  reacts quickly with  $\text{NO}$  and  $\text{NO}_2$ , but the rate constant for reaction with  $\text{O}_3$  is less than  $4 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ . *Ab initio* calculations of the potential energy surface for  $\text{FC(O)O} + \text{NO}$  and the heat of formation of  $\text{FC(O)O}$  and  $\text{FC(O)OH}$  will be presented. The stratospheric fate of  $\text{FC(O)O}$  and implications for ozone are discussed.

Laser Photolysis/Laser-induced Fluorescence Kinetic Studies of the Reaction of OH  
with HCFCs over Extended Temperature Ranges

Philip H. Taylor, Tunchen D. Fang, and Barry Dellinger

Environmental Science and Engineering  
University of Dayton  
Dayton, OH 45469-0132  
E-Mail: [Environ@udavxb.oca.udayton.edu](mailto:Environ@udavxb.oca.udayton.edu)

Submitted for Poster Presentation at the 7th BOC Priestley Conference  
(c/o American Chemical Society)  
June 24-27, 1994  
Bucknell University  
Lewisburg, PA

Abstract

It is widely accepted that photochemically produced chlorine and bromine from anthropogenic releases of chlorofluorocarbons (CFCs) is depleting the ozone layer in the earth's stratosphere. Partially as a result of a recent international accord, the replacement of perhalogenated CFCs with hydrogen containing CFCs (HCFCs) has been emphasized. Both production and disposal of HCFCs involves high-temperature, thermal processes that can result in formation of toxic reaction by-products, formation of ozone depleting CFCs, and emission of unreacted HCFCs. However, the high-temperature oxidation chemistry of these HCFCs is largely uncharacterized because of barriers imposed by past experimental techniques.

Radical initiation reactions, including those involving hydroxyl (OH), are primary reaction channels in the consumption of organic compounds under atmospheric and combustion conditions. We will present absolute rate coefficients of the reaction of OH with select C<sub>1</sub> and C<sub>2</sub> HCFCs over extended temperature ranges (e.g., 298 to 1000 K) using a laser photolysis/laser-induced fluorescence technique.

A comprehensive review of the literature indicates that the effects of  $\alpha$ - and  $\beta$ -fluorine substitution on the room temperature reactivity of C<sub>1</sub> and C<sub>2</sub> HCFCs are poorly understood. These findings indicate that additional study with a single apparatus is needed to better define the reactivity of these compounds. Our previous studies of the reaction of OH with chlorinated hydrocarbons over extended temperature ranges have also demonstrated that curvature in Arrhenius plots plays an important role in determining the reactivity of these compounds at elevated temperatures. The degree of curvature for the similar reactions of OH with C<sub>1</sub> and C<sub>2</sub> HCFCs and its impact on the reactivity of these compounds at elevated temperatures will also be presented. The high-temperature rate measurements will also serve as a basis for further improvement of semi-empirical modeling approaches of OH reactivity.

Kinetics of Hydrazine Fuel Reactions with Tropospheric O<sub>3</sub>

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The Aerospace Corporation,  
P.O. Box 92957, Los Angeles, CA 90009

Room temperature rate coefficients for the reactions of N<sub>2</sub>H<sub>4</sub>, CH<sub>3</sub>NN<sub>2</sub>H<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>N<sub>2</sub>H<sub>2</sub> with O<sub>3</sub> have been measured in a flow tube apparatus. The reaction rate for N<sub>2</sub>H<sub>4</sub> is more than an order of magnitude slower than that of the methylated hydrazines. The implications of the experimental results with respect to modelling the dissipation of launch site hydrazine spills have been estimated using a standard gaussian point source model. The effect of tropospheric water vapor on the hydrazine-ozone reaction rate has also been investigated.

Modelling HCl vapor adsorption on ice surfaces with the Density Functional Theory

Julio F. Caballero, Incarnate Word College  
 Division of Nursing, Mathematics  
 and Natural Sciences  
 4301 Broadway  
 San Antonio, Texas, 78209

Perla B. Balbuena, Chemical Engineering Department  
 University of Texas at Austin  
 Austin, Texas, 78212

The density functional theory (DFT) was used to calculate the isotherms and uptake of HCl vapor on ice. Ice is modelled as a non-polar surface without preferred sites or structure. The fluid surface interaction is based on an integrated Lennard-Jones (L-J) 10-4-3 potential and the fluid-fluid on L-J parameters based on viscosity data. We have chosen the DFT approach of Tarazona's (1) for inhomogeneous fluids. Calculation results show the rapid increase of the amount of HCl adsorbed at pressures and temperatures of atmospheric interest. HCl uptake calculations show good agreement with experimental data (2).

(1) Tarazona, P., Phys. Rev. A, 31, 2672(1985).

(2) Chu L., Leu M. and Keyser L.; J. Phys. Chem., 97, 7779(1993) and references therein.

OZONOLYSIS OF STILBENE, AN ORGANIC CHEMISTRY EXPERIMENT  
 J.J.Thomas, Dept of Science, Mt. St. Mary's College, Emmitsburg, MD. 21727

In this experiment air passing over a mercury vapor lamp generates the ozone to cleave stilbene, and the disappearance of stilbene is observed with the UV spectrometer.

Stilbene is used as a model to illustrate the ozonolysis of terpenes and other alkenes in the troposphere. A discussion of the experiment touches upon several principles of atmospheric photochemistry including the role of sunlight, NO and free radicals in the generation of ozone and the concerted nature of the cycloaddition of ozone to the double bond.



### A Study of Interferences in Ultraviolet and Chemiluminescence Ozone Monitors

E.E. Hudgens, T.E. Kleindienst, ManTech Environmental Services, Inc., F.F. McElroy, USEPA, and W.M. Ollison, American Petroleum Institute

Water vapor at ambient humidities positively biases dry calibrated ozone chemiluminescence monitors and exacerbates positive and negative interferences in ultraviolet instruments. Aromatic compounds and their oxidation products may show positive interferences in UV monitors during peak seasonal ozone conditions. High humidity also appears to reduce scavenging efficiency in some UV ozone scrubbers leading to negative monitoring errors. Anomalous scrubber behavior in the field has been studied in various failure modes under laboratory conditions and procedures for determining defective scrubbers evaluated. Ultraviolet instrument sensitivity to various aromatic ozone precursor species has been investigated under dry and humid conditions.

### Study on Ethylene and Hydroxyl-Ethyl Radical Oxidation in the Atmosphere: Ethylene + OH and C<sub>2</sub>H<sub>5</sub>CH<sub>2</sub>OH, CH<sub>3</sub>C-HOH + Oxygen

Wen-Chiun Ing, Lev N. Krasnoperov and Joseph W. Bozzelli,  
Department of Chemistry, Chemical Engineering and Environmental Sciences  
New Jersey Institute of Technology, Newark, NJ 07102.

#### Abstract

The initial reactions of ethanol under atmospheric conditions are loss of a H atom via abstraction reaction to form the hydroxyl ethyl radicals C<sub>2</sub>H<sub>5</sub>CH<sub>2</sub>OH and CH<sub>3</sub>C-HOH. The addition reaction of OH radical with ethylene also forms the 2-Hydroxyl-Ethyl radical. The reversible OH addition reaction and the subsequent reactions of C<sub>2</sub>H<sub>5</sub>CH<sub>2</sub>OH, CH<sub>3</sub>C-HOH with molecular oxygen are important steps in the oxidation of ethylene and ethanol in the atmosphere. These reactions are pressure and temperature dependent, with a chemical activation fall-off analysis needed to extrapolate the elementary rate constants measured at low pressures to atmospheric conditions. In this study a quantum version of Rice-Ramsperger-Kassel theory (QRRK) incorporating a modified strong collision approach was used to evaluate energy dependent rate constants,  $k(E)$ , for different channels. Input information required for the QRRK calculations (set of frequencies or Cp(T)) was obtained from literature data as well as by Group Additivity.

Potential energy diagrams of the reactions and thermodynamic properties ( $\Delta H^\circ_{298}$ ,  $S^\circ_{298}$  and Cp(T)'s) of reactants, intermediates and products are calculated using Group Additivity techniques (for  $\Delta H^\circ_{298}$ ) and semi-empirical Molecular Orbital (MO), AM1/UFF SCF method (for  $S^\circ_{298}$  and Cp(T)'s).

Rate constants for elementary reaction steps (input parameters to the QRRK computer code) are taken from literature or estimated using Transition State Theory and principles of thermochemical kinetics. Apparent rate constants are calculated for conditions of atmospheric oxidation as well as for other temperature and pressure regimes.

The results for atmospheric conditions are compared with available experimental data. Results for the CH<sub>3</sub>C-HOH + O<sub>2</sub> system are also compared with QRRK analysis and experimental data on the C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub> and the CH<sub>2</sub>O + HO<sub>2</sub> reactions systems. Analysis indicates that the experimental kinetic data on CH<sub>3</sub>C-HOH + O<sub>2</sub> cannot be explained unless a hydrogen-bonded complex is incorporated into the potential energy diagram and reaction system.

Results of this study confirm the importance of the hydrogen bonded complex for this reaction system (CH<sub>3</sub>C-HOH + O<sub>2</sub>) and suggest the possible importance of such complexes in other, similar, systems. The reaction description is based entirely on "complex formation" mechanism without "direct reaction". Results of these calculations, based on limited, low-pressure and narrow temperature range experimental data, can be used in combustion models over a wide temperature and pressure range.

## REACTION OF OH RADICAL WITH C<sub>2</sub>H<sub>3</sub>Cl: REACTION PATHWAY ANALYSIS

Vengun Ho and Joseph W. Bozzelli

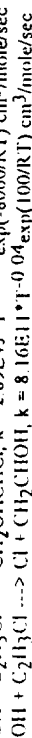
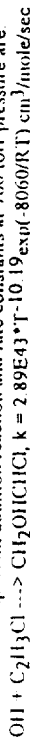
Dept. of Chemical Engineering, Chemistry, and Environment Science  
New Jersey Institute of Technology, NJ 07102

### Abstract

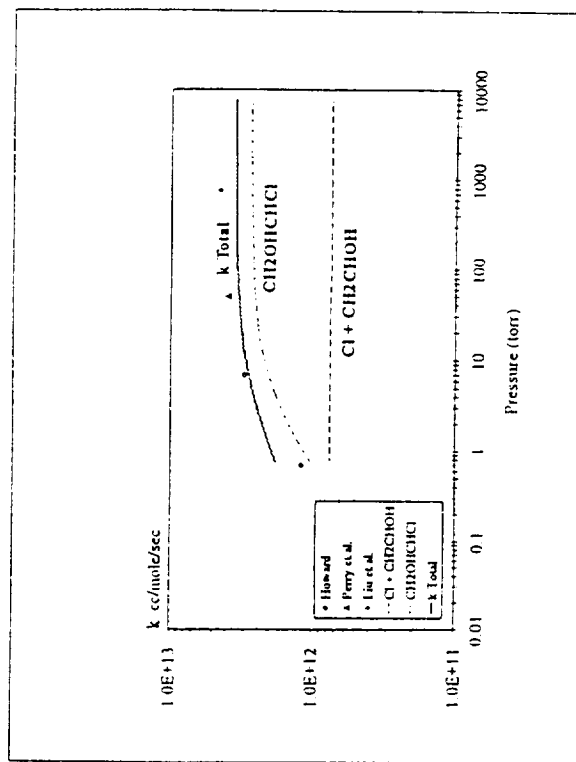
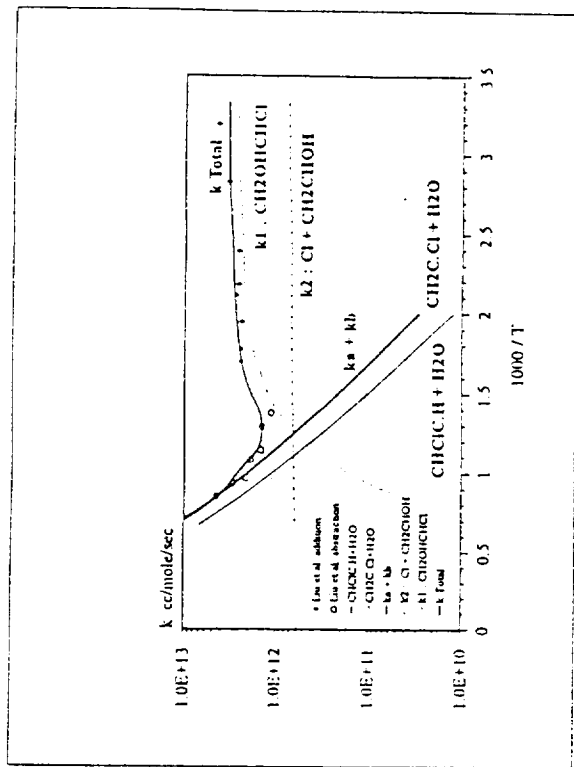
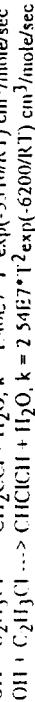
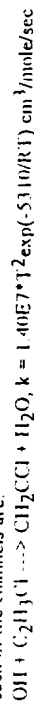
The gas phase reactions of OH radicals are important in combustion and incineration of chlorinated hydrocarbon (CHCs) as well as in atmospheric photochemistry. In combustion environments, OH is often the active radical present in the highest concentrations, where it initiates breakdown of hydrocarbons (HCs), adds to chlorinated olefins effecting Cl elimination, and it is also important in CO burnout producing CO<sub>2</sub> plus energy, plus H atoms. In atmospheric chemistry, OH is probably the most important active species. It abstracts hydrogen atom from saturated hydrocarbons forming HC radicals, which then react with O<sub>2</sub> and then NO sequentially, forming intermediates that contribute to photo-chemical smog. OH radical also adds to unsaturated hydrocarbons and oxy hydrocarbons forming radicals under atmospheric conditions, which then further react with O<sub>2</sub> and NO. Previous studies on OH radical reaction with unsaturated hydrocarbons such as vinyl chloride as well as this analysis, show that addition reaction is predominant at low temperature, while abstraction of H atom becomes important at high temperatures.

There are two distinct carbon atom sites in vinyl chloride where addition of OH may occur and two different types of H atoms where abstraction can occur. It would be helpful in both combustion and atmospheric modeling, to know the rate constants and specific reaction pathways for reaction of OH in each of the above four cases. In this work, we present analysis of the addition and abstraction reactions to the two carbon atom sites in vinyl chloride. The addition reactions of vinyl chloride with hydroxy radical have been analyzed using thermochemical analysis and a statistical chemical activation formalism based on a recently improved Quantum version of RRK Theory (QRRK) with a modified strong collision approach. The two abstraction paths have been analyzed by using Evans-Polanyi relation for activation energies and Transition-State-Theory for Arrhenius A factors. Thermodynamic parameters of the intermediate radicals and products are also listed.

Rate constant and reaction paths are predicted versus temperature and pressure and compared to experiment with good agreement in all cases. The calculations serve as useful estimates for rate constants and reaction paths in applications of combustion and atmospheric modeling (pressure and temperature), where experimentally data are not available. We evaluate and recommend rate constants over wide pressure and temperature range for OH addition and OH abstraction of H atom from the two distinct sites on vinyl chloride. The important addition reaction and rate constants at 760 torr pressure are:



Abstraction reactions are not dependent on pressure. Recommended rate constants for each of the channels are:



Pathways and Kinetic Estimation of Benzene Oxidation in the Atmosphere:  
Benzene + OH and the Adduct (Hydroxyl-2,4-cyclohexadienyl) + O<sub>2</sub>

Tsan H. Lay and Joseph W. Bozzelli,  
Chemical Engineering, Chemistry and Environmental Science,  
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Abstract

The reversible addition reaction of OH radical with Benzene to form the Hydroxyl-2,4-cyclohexadienyl (Cy.C<sub>6</sub>H<sub>6</sub>OH) adduct and the subsequent reactions of (Cy.C<sub>6</sub>H<sub>6</sub>OH) with O<sub>2</sub> are important initial steps of Benzene oxidation in the atmosphere. The OH addition, the reaction of O<sub>2</sub> with the hydroxyl-2,4-cyclohexadienyl to form Hydroxyl-2-peroxy-4-cyclohexenyl (CyOO.C<sub>6</sub>H<sub>6</sub>OH), are chemical activation reactions and are a function of both pressure and temperature. We evaluate the kinetics of these reaction systems at various P & T using a quantum version of Rice-Ramsperger-Kassel theory (QRRK) and a modified strong collision approach.

Potential energy diagrams of the reactions and thermodynamic properties ( $\Delta H^\circ$ ,  $r_{298}^\circ$ ,  $S^\circ_{298}$  and Cp(T)'s) of reactants, intermediates and products are calculated using Group Additivity techniques (for  $\Delta H^\circ$ ,  $r_{298}^\circ$ ) and semi-empirical Molecular Orbital (MO), AM1/UFF SCF method (for  $S^\circ_{298}$  and Cp(T)'s).

Rate constants for elementary reaction steps are determined from literature values or estimated from Transition State Theory and principles of thermochemical kinetics. Apparent rate constants are calculated for conditions of atmospheric oxidation as well as other temperature and pressure regimes. A short reaction mechanism is developed with reverse reaction rates from species thermodynamic parameters and microscopic reversibility. The results for atmospheric conditions are compared with available experimental data. Calculated kinetic and mechanistic data in this study can be used in modeling of photochemical oxidation of combustion and aromatic compounds in atmosphere. Results show that equilibrium levels of Cy.C<sub>6</sub>H<sub>6</sub>OH (the adduct from benzene + OH) react with O<sub>2</sub> and other active species in the system to effect conversion.

Heterogeneous Chlorine Chemistry in the Polar Stratosphere

Liang T. Chu<sup>1</sup>, Ming-Taun Leu<sup>2</sup>, and Leon F. Keyser<sup>2</sup>

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State University of New York, Albany, NY 12201-0509

<sup>2</sup>Jet Propulsion Laboratory  
California Institute of Technology  
Pasadena, CA 90019

Heterogeneous reactions occurring on the surface of Polar Stratospheric Clouds (PSCs) have played an important role in the depletion of ozone. In this study, we investigated the uptake of HCl in ice and nitric acid films which simulate PSCs and heterogeneous reactions of HOCH<sub>2</sub>Cl(s) → Cl<sub>2</sub>, H<sub>2</sub>O(s) and ClONO<sub>2</sub> + HCl(s) → Cl<sub>2</sub> + HNO<sub>3</sub>(s) on ice films. These studies were performed in a flow reactor using a differentially pumped mass spectrometer and experimental conditions mimic polar stratospheric clouds. The results shed light on the reaction mechanism and showed how the cloud surface played an important role in these reactions. The implication of these reactions to atmospheric chemistry will be addressed.

GASWATER UPTAKE STUDIES FOR REDUCED SULFUR COMPOUNDS USING A NEW BUBBLE COLUMN APPARATUS. E. Swartz, W. D. DeBruyn, J. Hu, J. A. Shorter\*, and P. Davidovits, Department of Chemistry, Merck Chemistry Center, Boston College, Chestnut Hill, MA 02167 and D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, Center for Chemical and Environmental Physics, Aerodyne Research, Inc., Billerica, MA 01821

Ocean produced reduced sulfur compounds including dimethylsulfide (DMS), hydrogen sulfide (H<sub>2</sub>S), carbon disulfide (CS<sub>2</sub>), methyl mercaptan (CH<sub>3</sub>SH) and carbonyl sulfide (OCS) deliver a sulfur burden to the atmosphere which is roughly equal to about half of the sulfur oxides produced by fossil fuel combustion. These species and their oxidation products dimethyl sulfoxide, dimethyl sulfone and methanethiolic acid dominate aerosol and CCN production in clean marine air. The multiphase chemical processes for these species must be understood in order to study the evolving role of combustion produced sulfur oxides over the oceans. Using a newly developed bubble column apparatus, detailed uptake studies have been completed for the reduced sulfur species DMS, H<sub>2</sub>S, CS<sub>2</sub>, CH<sub>3</sub>SH and OCS. In the apparatus a low pressure gas flow, carrying trace gas diluted in helium carrier gas, is 'bubbled' through a flask containing 3.5 liters of temperature controlled liquid. The outlet gas flow is then sampled by a differentially pumped mass spectrometer. The position of the bubble injector which determines the gas/liquid contact time, is computer controlled by means of a stepping motor. The outlet gas density is measured as a function of the distance the bubbles pass through the liquid. A non-linear fit to a numerical model yields values of  $k$  (the Henry's law coefficient) in the range 0.01 to 2 M/atm and values of the product  $hk/2$  (where  $k$  is the liquid phase reaction rate constant) in the range 0.1 to 200. Uptake studies were performed as a function of temperature, pH, ionic strength (i.e., NaCl and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> concentrations) and H<sub>2</sub>O<sub>2</sub> concentration. The results yielded Henry's law coefficients and the "sailing out" Setchenow coefficients for the species.

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## DIRECT MEASUREMENT OF THE O(<sup>3</sup>P) REACTION RATE CONSTANTS WITH SELECTED BIOGENIC HYDROCARBONS

Suzanne E. Paulson

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### Abstract

The rate constants for the reaction of O(<sup>3</sup>P) with the biogenic hydrocarbons Δ<sup>3</sup>-carene, α-pinene, and isoprene have been measured for the first time using a direct method. O(<sup>3</sup>P) was generated from the pulsed photolysis of NO<sub>2</sub> at 308 nm, and measured by resonance fluorescence at 131 nm. Rate constants at room temperature for the biogenics are similar; 3.3±0.6x10<sup>-11</sup>, 3.7±0.7x10<sup>-11</sup>, and 3.4±0.6x10<sup>-11</sup> cm<sup>3</sup>molec<sup>-1</sup>s<sup>-1</sup>, for Δ<sup>3</sup>-carene, α-pinene, and isoprene, respectively. The rate constant for the reaction of O(<sup>3</sup>P) with NO<sub>2</sub> was also measured with the same method, and this value is within 7% of the currently recommended value.

The Reaction  $O(^3P) + HOBr$ : Temperature dependence of the rate constant and importance of the reaction as an HOBr stratospheric loss process

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Relatively little is known about the role of HOBr in stratospheric or tropospheric chemistry.

In the troposphere, interest in HOBr chemistry has centred on its uptake on aerosols and subsequent condensed phase chemistry. Potentially in the stratosphere, HOBr could act as a temporary reservoir for BrO<sub>2</sub> compounds. Recently, the first direct measurements for the main HOBr stratospheric formation reaction HO<sub>2</sub> + BrO has found it to be 6 times larger than previously thought. In this work we have investigated a possible chemical stratospheric loss process for HOBr, the reaction between O(<sup>3</sup>P) and HOBr. The absolute rate constant for the reaction O(<sup>3</sup>P) + HOBr has been measured between T=233K and 423K using the discharge-flow kinetic technique coupled to mass spectrometric detection. The value of the rate coefficient at room temperature was  $(2.5 \pm 0.5) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and the derived Arrhenius expression is  $(1.4 \pm 0.5) \times 10^{-10} \exp\{(-430 \pm 260)/T\}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Implications for HOBr loss in the stratosphere have been tested using a 1D photochemical box model.

With the inclusion of the rate parameters and products (assumed to be OH + BrO) for the O + HOBr reaction, calculated concentration profiles of BrO increase by up to 33% around z = 35km. This result clearly indicates the need to include O + HOBr in global atmospheric chemistry models, particularly ones pertaining to the upper stratosphere. The inclusion of the O + HOBr reaction does not directly affect ozone depletion at these altitudes which is dominated by the HO<sub>2</sub> cycles. A degree of uncertainty exists owing to the undetermined photolysis rate of HOBr.

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## STRATOSPHERIC OZONE MONITORING IN ITALY OVER THE PAST 35 YEARS

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Atmospheric ozone evinces a marked variability related to both latitude and season as well as fluctuations over longer time periods that are mainly caused by quasi-biennial oscillations (QBO) and solar cycles. In addition to these periodical changes, there are disruptions both natural, like volcanic eruptions, and artificial, like those assumed to be responsible for the so-called Antarctic ozone hole.

Stratospheric ozone monitoring began in Italy during the late 1950s at stations in south-central areas of the country - Cagliari, Naples, Messina, Vigna di Valle - with Dobson spectrophotometers. These instruments measure ozone-induced absorption of solar radiation in UV wavelength pairs and enable ozone column content to be determined.

Vertical profile measurements of ozone concentration were taken from February 1967-July 1980 at the Cagliari-Elmas Observatory and since 1991 have been taken at the San Pietro Capofiume weather station near Bologna. Both of these stations used and are using balloon-borne sondes fitted with electrochemical cells (ECC) and conventional weather radio-sondes to measure partial ozone pressure and atmospheric pressure, temperature and relative humidity up to a 35-40 km altitude. Simultaneous measurements of total ozone via Dobson spectrophotometer provide the mean sonde-Dobson instrument normalization factor. The present study reports the total ozone column and vertical profile data for the measurement period and compares them to those taken by satellite (TOMS, SAGE I and II).

## TROPOSPHERIC OZONE CONTINUOUS MEASUREMENTS OVER THE OCEANS FROM 54°N TO 41°S

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Shipboard measurements of tropospheric ozone are highly representative of lower-atmosphere conditions; this position is supported by the fact that surface destruction of ozone over the oceans is approximately one-tenth of that over the land and hence shipboard sampling can be held as base-line.

As part of Italian Research Program in Antarctica (PNRA) data of tropospheric trace gases concentration and airborne particles sampling are executed on board during the cruise 1991-92 of R/V OGS Explora, sailed from Bremerhaven (53N, 8E) to Wellington (41S, 15W).

The ozone data presented were recorded by a probe-equipped Dasibi RS1003, UV-absorber analyser, installed under a protective bell on the flying bridge. The data were processed via moving averages for one-hour time interval and then averaged over an interval of one degree of latitude. The ozone concentration show a latitudinal distribution with higher ozone values in the mid-latitudes of the both emispheres and a pronounced equatorial minimum. A least-square regression is used to estimate the latitudinal gradients. Calculated ozone lifetimes show no significant differences between hemispheres, i.e. ten days in the northern and nine days in the southern.

**CORRELATION BETWEEN THE CONCENTRATION OF OXIDIZING AND REDUCING GASES IN THE ATMOSPHERE AND THE GENOTOXIC ACTIVITY OF AIRBORNE PARTICULATE MATTER**

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In this study the correlation between genotoxic activity of airborne particulate matter (APM) and atmospheric concentrations of NO, SO<sub>2</sub>, CO, NO<sub>2</sub>, ozone, and hydrocarbons was investigated. Samples were taken at eight sites once a month (for one week) over one year. For each site we determined the genotoxic activity (Ames Test, Comet Assay) of the APM and the concentration of the above mentioned noxious gases. The closest correlation was found between mutagenic activity and the concentration of NO, CO and hydrocarbons. For ozone a reverse result was found, respectively. Although mutagenic activity of APM is obviously correlated to the occurrence of reducing gases, the majority of the genotoxic activity can be shown in the oxidized fraction of the organic air-extract.

**Hydroperoxides in the Marine Troposphere over the Atlantic Ocean**

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**Abstract**

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and organic hydroperoxides (ROOH) were measured on board of the *Polarstern RV* during its cruise across the Atlantic Ocean from 20 October to 12 November 1990 (54°N to 51°S latitude) by the enzyme fluorometric method. The H<sub>2</sub>O<sub>2</sub> mixing ratio varied from below the detection limit of about 0.12 ppbv up to 3.89 ppbv, showing a latitudinal dependence with generally higher values around the equator and decreasing values poleward. The shape of the latitudinal H<sub>2</sub>O<sub>2</sub> distribution agrees well with an analytical steady state expression for H<sub>2</sub>O<sub>2</sub> using the measured H<sub>2</sub>O and O<sub>3</sub> distribution and a wind dependent H<sub>2</sub>O<sub>2</sub> deposition rate. The ROOH mixing ratio varied from below the detection limit of about 0.08 ppbv up to 1.25 ppbv with qualitatively the same latitudinal dependence as H<sub>2</sub>O<sub>2</sub>. The observed ratio ROOH/(ROOH+H<sub>2</sub>O<sub>2</sub>) varied between 0.17 and 0.98 showing higher values at the lowest H<sub>2</sub>O<sub>2</sub> mixing ratios at high latitudes. The measured H<sub>2</sub>O<sub>2</sub> mixing ratio shows a significant diurnal variation with a maximum around 14:00 local time, explicable by a superposition of the photochemical H<sub>2</sub>O<sub>2</sub> production with a constant H<sub>2</sub>O<sub>2</sub> deposition rate. Four independent estimations of the average effective H<sub>2</sub>O<sub>2</sub> deposition rate inferred from the H<sub>2</sub>O<sub>2</sub> decrease in the night, from the midday H<sub>2</sub>O<sub>2</sub> production deficit (as derived from comparison with a photochemical model and from the daily ozone loss), and from the offset in the latitudinal H<sub>2</sub>O<sub>2</sub> distribution, were consistent. An episode of maximum H<sub>2</sub>O<sub>2</sub> concentration pointed to its formation in clouds.

### OH RADICAL INITIATED PHOTO-OXIDATION OF ALKANES: ISOMERISATION OF 2-HEXOXY RADICALS

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The OH radical initiated photo-oxidation of alkanes in the troposphere leads to the generation of alkoxy radicals. Alkoxy radicals may react further by decomposition, reaction with oxygen or by isomerisation. The relative importance of each reaction channel will greatly influence the product distribution and hence the potential of the parent organic compound to promote the generation of ozone in the troposphere.

We have studied the reactions of 2-hexoxy radicals in an irradiated Teflon bag smog chamber under simulated tropospheric conditions. The 2-hexoxy radicals were generated by the photolysis of 2-hexyl nitrite and the products were analysed using GC-MS and HPLC.

### The heterogeneous photochemistry of pyrene and perylene in non activated silica surfaces as a model of atmospheric particulate.

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The reactivity of atmospheric pollutants such as the polycyclic aromatic hydrocarbons (PAHs) adsorbed on a surface is actively being studied, since airborne particulate matter has shown significant mutagenic and carcinogenic activity of its extracts. These effects can not be attributed solely to well known PAH carcinogenic compounds, and possible thermal or photochemical transformation have been suggested. Photochemical reactions of pyrene and perylene on unactivated silica gel as a model of atmospheric particulate and initiated by simulated laboratory UV irradiation and sunlight have been investigated in our laboratory. Enhanced rates of degradation are seen in an oxygen rich atmosphere. The photodegradation is followed directly on the adsorbent by front-face emission spectroscopy, and from the absorption and fluorescence spectra of extracts of the irradiated samples. The degradation of the PAHs and formation of products have been determined using HPLC techniques with UV-visible and fluorescence detectors. Products formed have more polar character than the corresponding PAH since they elute at shorter retention times in reverse phase HPLC. A large number of the products retain the PAH main absorption and emission chromophore incorporating oxygen containing groups into the PAH frame. This project is sponsored by EPA grant R816975-02-0.



NEAR ULTRAVIOLET PHOTODISSOCIATION DYNAMICS OF METHANETHIOL ( $\text{CH}_3\text{SH}$ )

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## ABSTRACT

The technique of H Rydberg atom photofragment translational spectroscopy has been applied to a high resolution study of the primary photochemistry of methanethiol ( $\text{CH}_3\text{SH}$ ) following excitation at a series of wavelengths between 274 and 204nm. In accord with previous studies of this molecule, excitation within its first ( $1^1\text{A}''-\tilde{\text{X}}^1\text{A}'$ ) absorption continuum is shown to result in S-H bond fission. Spectral analysis yields a refined value for the bond dissociation energy:  $D_0^0(\text{CH}_3\text{S-H}) = 30250 \pm 100 \text{cm}^{-1}$ . The resulting  $\text{CH}_3\text{S}(\tilde{\text{X}})$  fragments are deduced to carry only modest vibrational excitation, distributed specifically in the  $\nu_3$  (C-S stretching) mode and in one other mode having a wavenumber of  $\sim 1040 \text{cm}^{-1}$ . We associate this latter mode with bending of the  $\text{CH}_3$  moiety in the plane containing the C and S nuclei and the lobe of the unpaired electron which was originally involved in the S-H bond. Decreasing the excitation wavelength ( whilst remaining within the first absorption continuum) results in an increase in both the vibrational and rotational excitation of the  $\text{CH}_3\text{S}(\tilde{\text{X}})$  fragments, but a decrease in the relative yield of the upper ( $2^1\text{A}''-\tilde{\text{X}}^1\text{A}'$ ) spin-orbit component. Excitation at still shorter excitation wavelengths accesses the second ( $2^1\text{A}''-\tilde{\text{X}}^1\text{A}'$ ) absorption band of  $\text{CH}_3\text{SH}$ . The  $\text{CH}_3\text{S}$  fragments resulting from S-H bond fission at these excitation wavelengths are observed to carry very much higher levels of vibrational excitation in the above two modes. Evidence for the competing C-S bond fission channel is provided by observation of H atoms attributable to secondary photolysis of both  $\text{SH}(\tilde{\text{X}})$  and  $\text{CH}_3(\tilde{\text{X}})$  fragments.

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