

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

ALB

Date: 11/16/78

Project Title: A Kinetics Investigation of Several Key Tropospheric Chemical Reactions

Project No: B-525 Green acid

CO-Project DirectorS: Dr. A. R. Ravishankara and Dr. P. H. Wine

Sponsor: National Science Foundation

Agreement Period: From 10/15/78 Until 3/31/80 (Grant Period)

Type Agreement: Grant No. ATM-7810092

Amount: \$57,700 NSF
3,037 GIT (E- 862-010)
\$60,737 TOTAL

Reports Required: Annual Progress Report (if grant is extended); Final Project Report

Sponsor Contact Person (s):

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Defense Priority Rating: n/a

Assigned to: ASL/EEAD (School/Laboratory)

COPIES TO:

- Project Director
- Division Chief (EES)
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- Project Code (GTRI)
- Other Mr. F. H. Huff (info)

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT TERMINATION

Date: 7/7/81

Project Title: A Kinetics Investigation of Several Key Tropospheric Chemical Reactions

Project No: B-525

Co- Project Director: Dr. A. R. Ravishankara and Dr. P. H. Wine

Sponsor: National Science Foundation

Effective Termination Date: 3/31/81

Clearance of Accounting Charges: 3/31/81

Grant/Contract Closeout Actions Remaining:

- Final Invoice and Closing Documents
- Final Fiscal Report (FCTR)
- Final Report of Inventions (if possible)
- Govt. Property Inventory & Related Certificate
- Classified Material Certificate
- Other _____

Assigned to: EML/PSD ~~(School)~~ Laboratory)

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Other: _____

PROGRESS REPORT FOR THE PERIOD 10/78 - 3/80

During the first 18 months of our NSF program we have studied the kinetics of three important OH radical reactions as a function of temperature and pressure:



In addition, two methylperoxy radical reactions,



and



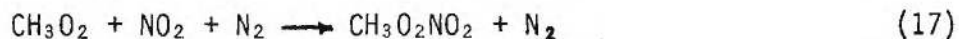
have been studied at 298K.

Reaction (12) was studied over a wide range of experimental conditions. A total of 57 bimolecular rate coefficients were measured. In the course of this study, the sensitivity of our flash photolysis-resonance fluorescence apparatus was improved significantly, thus allowing data to be obtained at N_2 pressures up to 225 Torr (initial OH concentrations of $< 3 \times 10^{11}$ per cm^3). Our results are in excellent agreement with those obtained by Anastasi and Smith¹ and, therefore, greatly reduce the uncertainty in $k_{12}(P,T)$ under atmospheric conditions. Our studies of Reactions (13) and (14) were recently completed. The improvements in apparatus sensitivity which were realized in the study of Reaction (12) were crucial to the studies of Reactions (13) and (14) because very low OH concentrations had to be employed in order to avoid secondary reactions

of COS/CS₂ photofragments with OH. The results show that both k₁₃ and k₁₄ are much slower than previously believed;^{2,3} it now appears that neither reaction is important in tropospheric sulfur chemistry. A reprint of a recent publication describing the study of Reaction (12) and preprints describing the investigations of Reactions (13) and (14) are attached as Appendices A-C.

Reaction (15) was studied using laser photolytic production of CH₃O₂ followed by time resolved laser induced fluorescence detection of the NO₂ product. This experimental technique was developed as part of the current program. Experimental details and a summary of results are given in Appendix D. Our result, k₁₅ ~ 7.6 x 10⁻¹² cm³molecule⁻¹s⁻¹ is in excellent agreement with two other recent determinations.^{4,5} It suggests that CH₃O₂ radicals will, via Reaction (15), efficiently produce NO₂ and hence O₃ in both the polluted and the clean troposphere.

The study of Reaction (16) was carried out using a recently constructed laser flash photolysis-long path laser absorption apparatus (LFP-LPLA) which was first built to study the reaction



as a function of temperature and pressure. Our result, k₁₆ ~ 4.5 x 10⁻¹³ cm³molecule⁻¹s⁻¹ is in good agreement with another recent direct measurement by Sander and Watson.⁴ The investigation of Reaction (17), which was funded by the Federal Aviation Administration, is now complete and a preprint describing this work and the LFP-LPLA apparatus is attached as Appendix E. The LFP-LPLA apparatus gives us the capability to study many reactions which cannot be investigated using fluorescence probing techniques. The capabilities of the system will be further enhanced when we can replace the fixed frequency laser probe which is currently being employed with a tunable laser probe.

During the remaining six months of the present grant period we expect to determine the temperature dependence of k_{15} and study the kinetics of the reaction



as a function of temperature and pressure. In all experiments, time resolved detection of NO_2 by laser induced fluorescence will be used as the kinetic probe. As discussed in the original proposal, Reaction (18) will be studied under pseudo-zeroth order conditions. This means that the absolute concentration of the reactants and the NO_2 product must be measured. In the case of Reaction (15), determination of the absolute concentration of the CH_3O_2 reactant and the NO_2 product will allow the NO_2 yield to be determined. Over the past eighteen months, we have spent considerable time developing a laser flash photolysis-laser induced fluorescence apparatus which is adaptable to studies which require knowledge of absolute transient concentrations. The apparatus and its application to the study of Reaction (15) is described in a reprint which is attached as Appendix F. We had hoped to have this apparatus "on-line" several months ago, but encountered a long delay in obtaining a segmented aperture optical integrator with a suitable coating for high UV reflectance. This device, which converts the photolysis laser beam into one with a uniform spatial intensity distribution, allows us to produce known concentrations of reactive free radicals. It was delivered about one month ago (March 1, 1980) and meets specifications.

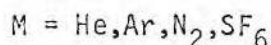
PLEASE READ INSTRUCTIONS ON REVERSE BEFORE COMPLETING

PART I-PROJECT IDENTIFICATION INFORMATION

1. Institution and Address Georgia Institute of Technology 225 North Avenue, N.W. Atlanta, Georgia 30332	2. NSF Program Atmospheric Chemistry	3. NSF Award Number ATM-78-10092
	4. Award Period From 10/15/78 To 3/31/81	5. Cumulative Award Amount \$114,943
6. Project Title A Kinetics Investigation of Several Key Tropospheric Chemical Reactions		

PART II-SUMMARY OF COMPLETED PROJECT (FOR PUBLIC USE)

This project involved the measurement of gas kinetic rate constants as a function of temperature for several key tropospheric reactions. The following four reactions were studied over the temperature range 240-370K



Our results for reactions (1) and (4) confirmed the results of earlier studies from other laboratories, thereby firmly establishing the role of reaction (1) in tropospheric HO_x and NO_x chemistry and the role of reaction (4) in hydrocarbon oxidation. The NO₂ product of reaction (4) was monitored in real time, allowing us to demonstrate by a direct technique that reaction (4) proceeds predominately via the channel giving CH₃O + NO₂. We found that reactions (2) and (3) were much slower than earlier measurements had indicated. This finding makes the role of reactions (2) and (3) in tropospheric sulfur oxidation very unclear. Based on CS₂ absorption cross section measurements and modeling calculations, we have proposed that the reaction of electronically excited CS₂ with O₂ may be a more important CS₂ oxidation mechanism than reaction (2).

In order to study reaction (4), a new laser-based extension of the conventional flash photolysis technique was developed. As mentioned above, the new technique permitted a direct measurement of a product yield; it also shows promise for studies of radical-radical reaction kinetics at tropospheric pressures.

PART III-TECHNICAL INFORMATION (FOR PROGRAM MANAGEMENT USES)

1. ITEM (Check appropriate blocks)	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM	
				Check (✓)	Approx. Date
a. Abstracts of Theses	X				
b. Publication Citations		X			
c. Data on Scientific Collaborators		X			
d. Information on Inventions	X				
e. Technical Description of Project and Results			X		
f. Other (specify)					
2. Principal Investigator/Project Director Name (Typed) A.R. Ravishankara F.A. Wine	3. Principal Investigator/Project Director Signature			4. Date June 24/81 June 24/81	

Publication Citations

1. "Flash Photolysis-Resonance Fluorescence Kinetics Study of the Reaction $\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$," Journal of Physical Chemistry, Volume 83, pp. 3191-3195, December 13, 1979.
Authors: P.H. Wine, N.M. Kreutter, and A.R. Ravishankara
2. "Rate of Reaction of OH with CS_2 ," Journal of Physical Chemistry, Volume 84, pp. 2499-2503, October 2, 1980.
Authors: P.H. Wine, R.C. Shah, and A.R. Ravishankara
3. "Rate of Reaction of OH with COS," Geophysical Research Letters, Volume 7, pp. 861-864, November 1980.
Authors: A.R. Ravishankara, N.M. Kreutter, R.C. Shah, and P.H. Wine.
4. "Kinetics of the Reaction of CH_3O_2 with NO ," Journal of Chemical Physics, Volume 74, pp. 2267-2274, February 15, 1981.
Authors: A.R. Ravishankara, F.L. Eisele, N.M. Kreutter, and P.H. Wine.
5. "Potential Role of CS_2 Photooxidation in Tropospheric Sulfur Chemistry," Geophysical Research Letters, Volume 8, pp. 543-546, May 1981.
Authors: P.H. Wine, W.L. Chameides, and A.R. Ravishankara

Scientific Collaborators

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Fred L. Eisele, Research Scientist II

Cheryl A. Gump, Undergraduate Student Assistant

Norman M. Kreutter, Undergraduate Co-op Student

Roger C. Shah, Undergraduate Student Assistant

*Professor Chameides collaborated with us on a modeling study of the atmospheric importance of CS₂ photo-oxidation. His contribution was funded by NASA while our contribution was funded by NSF.