

First Annual Progress Report
for the project

**Flow Tube Studies of Gas Phase Chemical Processes
of Atmospheric Importance**

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UPPER ATMOSPHERIC RESEARCH PROGRAM
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Flow Tube Studies of Gas Phase Chemical Processes of Atmospheric Importance

Objective:

The objective of this project is to conduct measurements of elementary reaction rate constants and photochemistry parameters for processes of importance in the atmosphere. These measurements are being carried out under temperature and pressure conditions covering those applicable to the stratosphere and upper troposphere, using the chemical ionization mass spectrometry turbulent flow technique developed in our laboratory.

The next section summarizes our research activities during the first year of the project, and the section that follows consists of the statement of work for the second year. Additional details concerning the projects listed in the statement of work were described in our original proposal.

Accomplishments:

Chemical kinetics studies of the OH + ClO reaction

A study of the OH + ClO reaction has been conducted using the turbulent flow technique with high-pressure chemical ionization mass spectrometry for the detection of reactants and products. The OH + ClO reaction has two potential product channels:



The large background level of HCl from the ClO source made it difficult to detect small amounts of HCl produced by reaction 1b. In using OD instead, we have been able to observe the production of very small concentrations of DCl ($\sim 10^9$ molecule cm^{-3}) over the experimental reaction time (~ 20 ms) which we have positively identified as coming from reaction 1b. Using OD, we investigated the overall rate and branching ratio (k_{1b}/k_1) of reaction 1 as a function of temperature and determined the branching ratio to be 0.06 ± 0.02 at 210 K and a pressure of 100 Torr. These results have already been published in the literature [*J. Chem. Soc., Faraday Trans.*, **93**, 2665 (1997)].

We are currently investigating ways to reduce the HCl background from the ClO source. ClO is produced by the reaction of Cl and O₃ in the movable injector. Chlorine atoms are formed by sending Cl₂ through a microwave discharge produced by a Beenakker cavity. We have determined that a significant amount of the HCl background from the ClO source was coming from trace impurities of H₂ in the helium sweep gas used to flush Cl₂ through the microwave discharge. Although 99.999 % pure helium was used, the manufacturer specifications indicate levels of H₂ up to 1 ppm. We have significantly reduced the HCl background from the ClO source by installing an “Aeronex” inert gas purifier that decreases H₂ impurities to sub-ppb levels. We have also found that switching to an argon sweep gas, instead of helium, increases the efficiency of the Cl₂ microwave dissociation, making it possible to produce the same amount of ClO using less Cl₂. Lower initial Cl₂ concentrations have also helped to reduce the HCl background in our system. Another source of HCl background was coming from the interaction of Cl atoms with the glass walls of the movable injector. We have greatly reduced this background contribution by switching to an injector made out of alumina.

We believe that the significant reductions of HCl background in our system will make it possible to determine the branching ratio of reaction 1 using OH instead of OD.

We are continuing to refine the quantitative measurement, but preliminary experiments indicate that the branching ratio for OH + ClO appears to be similar to our measured branching ratio for OD + ClO. In the next phase of our project, we will study the pressure dependence of the branching ratio for the OH + ClO reaction. We expect little, if any pressure effect, but we want to investigate it anyhow in order to better establish the reaction mechanism.

Chemical kinetics investigation of the ClO + NO₂ reaction

The rate constant for the reaction $\text{ClO} + \text{NO}_2 + \text{M}$ was measured between 150 and 600 Torr and at 298 and 213K using a turbulent flow technique with high pressure chemical ionization mass spectrometry for the detection of reactants. This work represents the first experimental evaluation of this rate coefficient at temperatures below 248K. The results are in excellent agreement with the values recommended by the NASA Panel for Data Evaluation (DeMore *et al.*, JPL Publication 97-4, 1997). An article describing our work has been accepted for publication in the Journal of Physical Chemistry.

Several groups have studied this reaction relatively recently at temperatures above ~250 K, concluding that chlorine nitrate, ClONO₂, is the only product, in disagreement with earlier suggestions that another isomer such as ClOONO was also formed (see, e.g., DeMore *et al.*). On the other hand, the formation of such an isomer would not have been observed in those studies if the ClO-ONO bond strength is less than ~15 kcal/mole, because at temperatures above 250 K the isomer would rapidly decompose regenerating the reactants ClO and NO₂. Our results indicate that no such weakly-bound isomer of chlorine nitrate is formed at significant rates at temperatures down to 213 K, since no unexpected increase in the rate of disappearance of ClO was observed at the lower temperatures.

Quantum yield for $O(^1D)$ production in the photolysis of O_3

The quantum yield for $O(^1D)$ production in the photolysis of ozone in the 290 - 320 nm wavelength range is being investigated using our CIMS- flow tube technique. A small diameter flow tube serves as the photolysis cell and as a light pipe; it is coupled to an arc-lamp monochromator radiation source. The purpose of this apparatus is to monitor with very high sensitivity small amounts of an end product generated by $O(^1D)$ in the flow tube, while scanning the photolysis wavelength with the monochromator.

The first phase of this process consisted in adapting one of our CIMS-flow tube apparatus to operate with very small overall gas flows. For our normal kinetics studies we utilize typically a 1"-diameter flow tube, and only a small portion of the flow is sampled, ionized and introduced into the mass spectrometer. For the photolysis project we are limited by the available radiation intensity, that is, by the photon flux; hence, we employ a flow tube with a diameter of only a few millimeters, and introduce the entire flow into the chemical ionization chamber. Furthermore, we have miniaturized this chamber using capillary tubes to transport the ions, so that a much larger fraction of the incoming reactant flow ends up being sampled by the mass spectrometer. We have successfully accomplished these modifications, and can now monitor species concentrations present in a greatly reduced flow with a sensitivity comparable to the one we have for our conventional large flow, large diameter tubes.

The first chemical system we are investigating consists of a mixture of ozone and nitrous oxide (N_2O); reaction of this species with $O(^1D)$ generates NO , which in turn reacts with the excess ozone to yield NO_2 . This species can in principle be detected with very high sensitivity by means of the CIMS technique, using SF_6^- as the ion reactant. A problem with this particular approach turned out to be that trace amounts of NO_2 cannot be monitored in the presence of a large excess O_3 , most likely because NO_2^- reacts rapidly

with O_3 to yield O_3^- . We attempted to destroy the large excess ozone with hot copper, but this process also affected significantly the trace amounts of NO_2 that needed to be monitored. Hence, we decided to test various alternate ion-molecule schemes; at present we are investigating positive ion formation and detection of NO_2^+ , since positive ozone ions are not stable. Other schemes to be tested include detection of CO_2 in a mixture of O_3 , H_2O and CO ; the $O(^1D)$ channel would generate OH radicals, which would in turn oxidize excess CO to CO_2 .

Intermediates in the atmospheric photo-oxidation of hydrocarbons

We have developed and assembled a fast-flow chemical ionization mass spectrometer apparatus designed to monitor positive ions in order to monitor intermediates in the atmospheric oxidation of hydrocarbons. This apparatus is similar to those we are employing for our gas phase reaction rate studies using mainly SF_6^- as a reactant ion; however, we modified the ion generation scheme, and are employing either a radioactive polonium source or a glow discharge source to produce O_2^+ ions. Furthermore, we have been able to improve the ion extraction interface coupled to the high vacuum quadrupole mass filter chamber: we designed an ion guide, placed inside the mass-spectrometer vacuum chamber and consisting of a central wire surrounded with a tube made out of copper screen. The wire and the screen are charged at opposite polarities in order to maintain a flow of positive ions towards the center of the tube, while accelerating the negative ions towards the screen. Neutral species are pumped through the screen with a diffusion pump; the net effect is to selectively and efficiently guide ions of the desired polarity between the entrance sampling orifice and the quadrupole rods of the mass spectrometer, over a distance of the order of ten centimeters. The overall performance of this interface turned out to be very satisfactory; we are now beginning to investigate various positive ion-molecule schemes to directly monitor hydrocarbon intermediates.

Statement of Work for the Second Year of the Project:

1. The flow tube - CIMS apparatus for photolysis studies will be further developed; several ion-molecule reaction schemes will be investigated to measure the quantum yield for $O(^1D)$ production in the photolysis of ozone as a function of wavelength and temperature.
2. The positive ion fast-flow CIMS apparatus will be utilized to measure rate constants for reactions of peroxy radicals (RO_2) with NO , NO_2 and/or HO_2 , after suitable development of appropriate ion-molecule detection schemes.
3. The fast flow CIMS apparatus operating in the negative ion mode will be utilized to investigate the effect of water vapor on various reactions of the HO_2 radical of atmospheric interest, such as $OH + HO_2$ and $HO_2 + HO_2$.

Publications:

1. Temperature dependence of the rate constant and branching ratio for the $OH + ClO$ reaction, J.B. Lipson, M.J. Elrod, T.W. Beiderhase, L.T. Molina and M.J. Molina, J. Chem. Soc., Faraday Trans., 93, 2665-2673, 1997.
2. Temperature and pressure dependence of the rate constant for the $ClO + NO_2$ reaction, C.J. Percival, G.D. Smith, L.T. Molina, and M.J. Molina, J. Phys. Chem., in press, 1997.

Budget For the Second Year*

	<u>Year 2</u>
Salaries and Wages (S&W)	
Principal Investigator (1 s.m.)	12,880
Research Associate (100% of 12 mos.)	30,900
1 Research Assistant (100%, 12 mos.)	16,790
1 Research Assistant (50%, 12 mos.)	8,400
Project Support Staff (15%, 12 mos.)	<u>3,500</u>
Subtotal S&W	72,470
Employee Benefits (EB)	
46.2% of S&W	<u>33,480</u>
Sub-total (S&W, EB)	105,950
Travel	1,500
American Chemical Society meeting for 1 person airfare - 800; subsistence - 500; misc. - 200	
Materials and Services	9,000
Liquid Nitrogen, Chemicals, Glassware, Hardware, Glass and Machine Shop Service	
Publications	1,600
Permanent Equipment	<u>7,000</u>
Total Direct Costs	125,050
Modified Total Direct Costs (MTDC)	118,050
Indirect Costs	<u>74,960</u>
(63.5% of MTDC)	
TOTAL	\$200,010

* Please note that this is the same budget that was submitted previously with the three-year proposal and approved for the multi-year grant by NASA Headquarters.

BUDGET SUMMARY

Year 2 From 1/1/98 to 12/31/98

	RECIPIENT'S COSTS	NASA USE ONLY	
	A	B	C
1. Direct Labor (salaries, wages, and fringe benefits)	105,950		
2. Other Direct Costs:			
a. Subcontracts	0		
b. Consultants	0		
c. Equipment	7,000		
d. Supplies (M&S)	9,000		
e. Travel	1,500		
f. Other (Publication)	1,600		
3. Indirect Costs	74,960		
4. Other Applicable Costs	0		
5. SUBTOTAL - Estimated Costs	200,010		
6. Less Proposed Costs Sharing (if any)	0		
7. Carryover Funds (if any)			
a. Anticipated amount			
b. Amount used to reduce budget	0		
8. TOTAL ESTIMATED COST	200,010		xxxxxxxxxxxxx
APPROVED BUDGET	xxxxxxxxxxxxx	xxxxxxxxxxxxx	

Instructions

1. Provide a complete budget summary sheet for year one and separate estimates for each subsequent year.
2. Recipient's estimated costs should be entered in Column A. Columns B and C are for NASA use only.
Column C represents the approved grant budget.
3. Provide as attachments detailed computations of estimates in each cost category with narratives required to fully explain proposed costs. See Page No. 2, Attachment C (over).