Second Annual Progress report
For the Project

Laboratory Studies of
Homogeneous and Heterogeneous Chemical Processes
of Importance in the Upper Atmosphere

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OBJECTIVE:

The objective of this study is to conduct measurements of chemical kinetics parameters for reactions of importance in the stratosphere and upper troposphere, and to study the interaction of trace gases such as HCl with ice surfaces in order to elucidate the mechanism of heterogeneous chlorine activation processes, using both a theoretical and an experimental approach. The measurements will be carried out under temperature and pressure conditions covering those applicable to the stratosphere and upper troposphere. The techniques to be employed include turbulent flow – chemical ionization mass spectrometry, and optical ellipsometry.

The next section summarizes our research activities during the second year of the project, and the section that follows consists of the statement of work for the third year.

ACCOMPLISHMENTS:

Reaction probability for $ClONO_2$ + HCl

Summary

We have modified our chemical ionization mass spectrometry (CIMS) fast flow tube apparatus to provide significantly higher sensitivity detection in order to investigate chlorine activation reactions under temperature and reactant concentration conditions applicable to the polar stratosphere. We have measured the reaction probability for the reaction

$$ClONO_2 + HCl(ads) \rightarrow Cl_2 + HNO_3(ads) \quad (1)$$
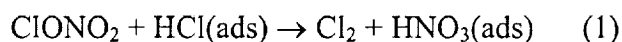
on smooth ice substrates. Studies were conducted at 200 K, with partial pressures of HCl between 10^{-7} and 10^{-6} Torr and $ClONO_2$ partial pressures between $5 \cdot 10^{-8}$ and $1 \cdot 10^{-6}$ Torr.

The ratio P_{HCl}:P_{ClONO2} was at least 3 in order to approach pseudo-first-order conditions. The reactive uptake coefficient was found to be dependent on HCl surface coverage, for the smaller P_{HCl} values. No dependence on the $ClONO_2$ partial pressure was observed in excess HCl.

Background

Our group and others have studied this reaction previously. In all cases a high reaction probability has been measured ($\gamma > 0.1$) and has not been observed to be a function of HCl or $ClONO_2$ partial pressure. Most of these previous studies have been conducted using low-sensitivity techniques, and most, if not all have been conducted using porous ice, which has a poorly characterized morphology and surface area.

Our recently modified CIMS detection scheme is sufficiently sensitive to HCl to allow sampling of sub-saturation coverages of HCl on ice. With an integration time of 200 msec, our sensitivity towards $ClONO_2$ is 10^6 molecule cm^{-3}, similar to the sensitivity towards HCl.

Measurements

For each reactive uptake experiment, the flow tube was evacuated and pre-cooled to 196 K and then the smooth ice film substrate was prepared by freezing from the melt. The helium carrier gas and chemical ionization flows were then established, bringing the flow tube to a total pressure of 1.75 Torr.

One moveable vacuum-jacketed injector was used for each reactant. These injectors were also heated resistively to counteract artifacts due to adsorption of reactants onto the injector walls. Heat flux from the injectors into the flow tube increased the flow tube temperature from the baseline 196 K to 200K.

Results

The reactive uptake coefficients, γ, were calculated as in our previous work. For values of $P_{HCl} > 2.7 \cdot 10^{-7}$ Torr, γ was found to be constant, with an average value of 0.06 (+0.1, -0.02). The reaction probability γ increased fairly smoothly with increasing P_{HCl}

for $1.8 \times 10^{-7} < P_{HCl} < 2.7 \times 10^{-7}$ Torr. Our results also show that there is no dependence of the efficiency of reaction (1) on $ClONO_2$ partial pressure.

We also measured the adsorption isotherm for HCl on smooth ice at 186 K. The saturation surface coverage was found to be around $3 - 4 \times 10^{13}$ molecule cm^{-2} for HCl partial pressures above 3×10^{-7} Torr.

We conclude that the efficiency of reaction (1) is dependent on the surface coverage of HCl. For values of $P_{HCl} < 3 \times 10^{-7}$ Torr, γ increases with increasing HCl surface coverage. Once saturation of the surface with HCl is reached, the reactive uptake coefficient levels off at a constant value, which is a factor of two or three smaller than the value measured earlier by us and by other groups on porous ice. We are in the process of re-measuring the reactive uptake coefficient on porous ice at low P_{HCl} to gain further insight into the origin of the discrepancy.

Theoretical studies of the interaction of HCl with the (0001) face of hexagonal ice

We have continued our theoretical studies of the interaction of HCl with ice, using Car-Parrinello molecular dynamics. We conclude that, in regions with a low surface density of dangling OH groups, HCl may be either ionically or molecularly adsorbed, but in regions with a high surface density of dangling OH groups, HCl is ionically adsorbed. Car-Parrinello molecular dynamics simulations indicate that HCl ionizes with essentially no barrier at stratospherically relevant temperatures at a surface site with two nearby dangling OH groups. The ionized form is 21 kJ/mol more stable than molecularly adsorbed HCl. Conversely, there is a barrier to dissociation of unknown magnitude in regions with a low OH density, and (at most) only a weak thermodynamic preference for dissociated HCl. A disordered ice surface exists below ionized, but not molecular, HCl. This work has been accepted for publication in Chemical Physics Letters.

Theoretical Study of the Interaction of HCl with the (001) Face of Crystalline Nitric Acid Trihydrate

Using density-functional-plane-wave-based and localized-orbital computational methods, we systematically examined the interaction of HCl with a low index face of nitric acid trihydrate (NAT). Out of 54 plausible binding sites, we identify only one site

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on the NAT (001) face that exhibits a high affinity for HCl. At this binding site, adsorbed HCl forms a strong H-O hydrogen bond with a NO_3^- ion and a weaker Cl-H hydrogen bond with the dangling OH group of a nearby H_2O molecule. We estimate that the interaction energy and enthalpy at 190 K corrected for zero-point energies is 23 and 25 kJ/mol, respectively. During a 1.0 ps Car-Parrinello molecular dynamics simulation, the adsorbed HCl molecule at this binding site does not dissociate, consistent with previously published theoretical studies reporting that HCl does not dissociate when interacting with only one dangling OH group on the (0001) face of ice Ih. In addition, when dissociated HCl is placed at this binding site and a geometry optimization is performed, molecular HCl is reformed.

Measurement of Radical Quantum Yields from Formaldehyde Photolysis

We have measured the quantum yield for the production of radical products, H and HCO, from the photolysis of formaldehyde (HCHO) directly at wavelengths from 269 nm to 339 nm. Measurements of the radical products were conducted using chemical amplification with subsequent detection by chemical ionization mass spectrometry (CIMS). We measured all yields at a pressure of 50 Torr, normalized to a quantum yield of 0.753 at 303.75 nm based on the recommendation of the NASA Data Panel for Data Evaluation. The quantum yields were measured with sufficient wavelength resolution ($\pm$ 0.62 nm, fwhm) to observe structure which had been previously unreported and is believed to provide evidence for a complicated competition amongst the various dissociation pathways to H + HCO, H +H + CO and H_2 + CO, as well as with quenching to the ground state. The quantum yields measured should aid in the calculation of formaldehyde photolysis rates in the troposphere and are estimated to result in increases of at least 8% in calculated H/HCO production.

This work has been submitted and accepted for publication in the Journal of Physical Chemistry A.

Statement of Work for the Third Year of the Project:

1. Gas phase studies of radical-radical reactions will continue to be carried out with the increased sensitivity flow tube – CIMS. The rate constants for the reactions of HO_2 with itself will be measured at low and high relative humidity.

2. The interaction of HCl vapor with ice will be investigated experimentally using the ellipsometric technique, to complement our flow-tub studies.

3. The interaction of HCl vapor with nitric acid trihydrate surfaces will be investigated experimentally and the role of relative humidity on the reaction probability for the $HCl + ClONO_2$ reaction will be elucidated at low and high HCl partial pressures.

Publications

1. Measurement of Relative Product Yields from the Photolysis of Dichlorine Monoxide (Cl_2O), Geoffrey D. Smith, Fransisco M.G. Tablas, Luisa T. Molina, and Mario J. Molina, *Journal of Physical Chemistry A*, **105**, 8658-8664, 2001.

2. First-principles molecular dynamics study of surface disordering of the (0001) face of hexagonal ice, Yves A. Mantz, Franz M. Geiger, Luisa T. Molina, Mario J. Molina and Bernhardt L. Trout, *Journal of Chemical Physics*, **113**, 10,733-10,743, 2000.

3. First-principles theoretical study of HCl adsorption on a hexagonal ice (0001) surface, Yves A. Mantz, Franz M. Geiger, Luisa T. Molina, Mario J. Molina and Bernhardt L. Trout, *Journal of Physical Chemistry A*, **105**, 7037-7046, 2001.

4. Measurement of Radical Quantum Yields from Formaldehyde Photolysis between 269 and 339 nm, Geoffrey D. Smith, Luisa T. Molina and Mario J. Molina, accepted for publication in *Journal of Physical Chemistry A,* 2001.

BUDGET SUMMARY

YEAR 3   From __1/1/2002__   To __12/31/2002__

| | RECIPIENT'S COSTS | NASA USE ONLY | |
	A	B	C
1. Direct Labor (salaries, wages, and fringe benefits)	94,476		
2. Other Direct Costs:	0		
a. Subcontracts			
b. Consultants	0		
c. Equipment	0		
d. Supplies	8,000		
e. Travel	2,600		
f. Other (Tuition, Publications, Shop Services)	23,120		
3. Indirect Costs	71,576		
4. Other Applicable Costs	0		
5. SUBTOTAL -- Estimated Costs	199,772		
6. Less Proposed Cost Sharing (if any)	0		
7. Carryover Funds (if any)			
a. Anticipated amount _____			
b. Amount used to reduce budget	0		
8. TOTAL ESTIMATED COST	199,772		xxxxxxxxxxxx
APPROVED BUDGET	xxxxxxxxxxxx	xxxxxxxxxxxx	

<u>Instructions</u>

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.