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

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OBJECTIVE:

The objective of this study was 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 with ice surfaces in order to elucidate the mechanism of heterogeneous chlorine activation processes, using both a theoretical and an experimental approach. The measurements were carried out under temperature and pressure conditions covering those applicable to the stratosphere and upper troposphere. The main experimental technique employed was turbulent flow – chemical ionization mass spectrometry, which is particularly well suited for investigations of radical-radical reactions.

ACCOMPLISHMENTS:

1. UPTAKE OF HCL VAPOR ON ICE SURFACES

Experimental procedure. In order to investigate the interaction of HCl with ice and chlorine activation reactions under temperature and reactant concentration conditions applicable to the polar stratosphere, we modified our chemical ionization mass spectrometry (CIMS) fast flow tube apparatus to provide significantly higher sensitivity detection than in our previous studies. Our current detection limit for HCl is 8×10^{-10} Torr for an integration time of one second with a unity signal to noise ratio.

Ice films were prepared either by freezing a thin film of liquid water prepared by wetting the cylindrical flow tube with de-ionized water (smooth ice), or by deposition of water vapor onto the cold flow tube (porous ice). The ice films were exposed to HCl as follows: with the injector positioned past the ice film close to the chemical ionization region and the front aperture, the background HCl sample signal was recorded over time. Then the HCl gas flow was established at a given rate, yielding a specific and well-controlled HCl concentration in the flow tube. When the sample ion signal was stable, the injector was quickly moved upstream and fixed at a given distance, while recording the HCl ion signal over time. Once the sample ion signal had recovered to its original level with the HCl gas flow present, the injector was pushed back downstream to the starting position. When the sample ion signal had decayed to its original level, the sample gas valve was closed and the ion signal was allowed to return to its background level. Integration of the observed ion signal versus time yielded the amount of HCl taken up by the ice.

HCl surface coverage. We measured HCl adsorption isotherms on smooth ice for HCl partial pressures up to 10^{-6} Torr and ice temperatures between 186 and 209 K. The results appear to indicate Langmuir-type isotherms, with a saturation surface coverage of the order of 10^{14} molec cm^{-2} on smooth ice, for HCl partial pressures above 3 x 10^{-7} Torr (see Figure 1). The results of this set of measurements can be interpreted either as conventional physical adsorption on th ice surface, or else as uptake in the surface layers to form a "quasi-liquid layer". As expected, the apparent surface coverage on the porous ice is several times larger, and depends on the water vapor deposition rate, i.e. the ice porosity. We analyzed the data using the conventional Langmuir model, which yields the Langmuir constant K_{ads}, and the free energy of adsorption. In principle, the interaction energy of HCl molecules with the ice surface –i.e., the isosteric enthalpy of adsorption– is given by the slope of a plot of the logarithm of the HCl partial pressure versus inverse temperature for constant surface coverage θ. This is a general conclusion obtained by thermodynamic considerations, and is independent of the type of isotherm characteristic of the system; it is similar to the interpretation of the Clausius-Clapeyron equation for vapor pressures:

$$\left(\frac{\partial \ln P_{HCl}}{\partial (1/T)}\right)_{\theta} = \frac{\Delta H_{ads}}{R}$$

It turns out, however, that there is significant scatter in the results, so that we are only able to infer a lower limit to the interaction energy of HCl with ice of ~30 kJ mol^{-1}. Most importantly, it appears that the ice surface is modified by exposure to HCl, so that subsequent exposures yield different surface coverage. Furthermore, a certain amount of HCl is *irreversibly* taken up by the ice, as observed previously by our group and others [e.g. Flückiger et al., 2000; Hynes et al., 2001]. Although some of this HCl might be migrating into the bulk solid, it appears that most of it remains close to the surface, and is more tightly bound than the portion that is reversibly adsorbed.

HCl Uptake at high P_{HCl} on smooth ice films. At 186 K and HCl partial pressures above 6 x 10^{-7} Torr, we observed HCl losses that are consistent with the formation of the HCl hexahydrate. When such higher HCl partial pressures are used, conventional, fast adsorption is observed at early times, but then a pronounced dip is observed in the signal vs. time trace, indicating that a secondary adsorption process is taking place.

We examined the possibility for hexahydrate formation for the second HCl adsorption plateau by measuring the water vapor pressure of several smooth ice films held between 188 K and 195 K as a function of HCl partial pressure in the flow tube. The results are shown in Figure 2. It can be seen that at each ice film temperature, the water vapor pressure remains at the equilibrium ice vapor pressure for small HCl pressures, and decreases for HCl partial pressures above 4 x 10^{-6} – 2 x 10^{-6} with slopes of 5.8 ± 0.4, 6.5 ± 0.5, and 5.9 ± 0.4. The Gibbs-Duhem relation indicates that these slopes represent the molar ratio of water to HCl, which in this case agrees well with the water-to HCl molar ratio of the HCl hexahydrate.

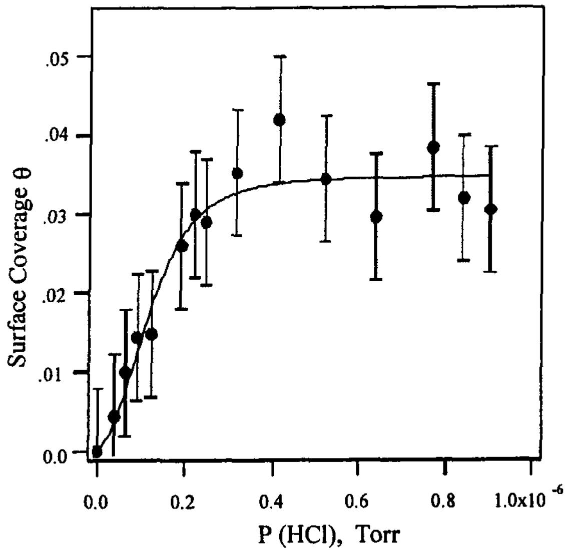

Fig. 1. HCl adsorption isotherm on ice formed by freezing from the melt, T_{ice} = 186 K. The surface coverage is given in arbitrary units.

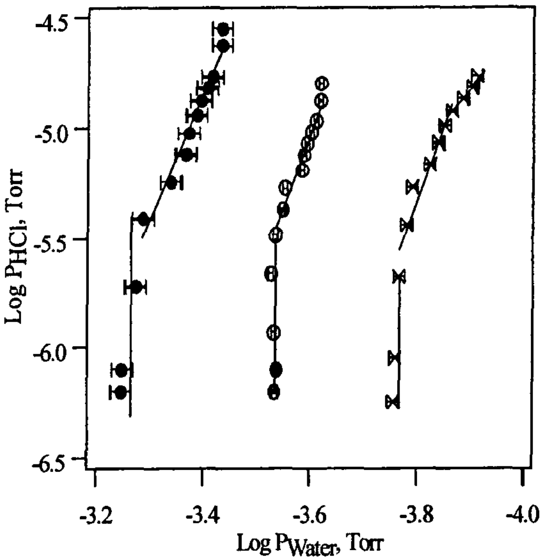

Fig. 2. Gibbs-Duhem plot of HCl pressure vs. water vapor pressure. Filled circles are for T_{ice} = 195 K, open circles are for T_{ice} = 191 K, and crosses are for T_{ice} = 188 K.

This finding corroborates the formation of HCl hexahydrate for the case of increased HCl uptake on ice held at 186 K, as shown in Figure 2, and is consistent with the HCl phase diagram published in our earlier work, in which we mapped the ice-HCl hexahydrate coexistence line [Woolridge et al., 1995]. We were not able to observe the formation of the hexahydrate on porous ice: we speculate that there is a significant nucleation barrier for the formation of this hydrate, so that the probability of forming large domains of this new phase is small for the porous ice. The reason is that the single-crystal size is probably much larger for the smooth ice, and a single nucleation event gives rise to the formation of the hexahydrate over a relatively large area.

2. REACTION PROBABILITY FOR $ClONO_2$ + HCl ON ICE

We measured the reaction probability for the reaction

$$ClONO_2 + HCl(ads) \rightarrow Cl_2 + HNO_3(ads) \qquad (1)$$

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.

Our group and others have studied this reaction previously. A large reaction probability was measured in all cases ($\gamma > 0.1$), and was not observed to be a function of HCl or $ClONO_2$ partial pressure. Several of these earlier studies were conducted using low-sensitivity techniques, and most have been conducted using porous ice, which has a poorly characterized morphology and surface area. With an integration time of 200 msec, our sensitivity towards $ClONO_2$ is 10^6 molec 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. The reaction probability γ increased fairly smoothly with increasing P_{HCl} for $1.8 x 10^{-7} < P_{HCl} < 2.7 x 10^{-7}$ Torr. Our results also show that there is no dependence of the efficiency of reaction (1) on $ClONO_2$ partial pressure.

We conclude that the reaction probability γ is dependent on the surface coverage of HCl. For values of $P_{HCl} < 3 \text{ x} 10^{-7}$ 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 about a factor of two smaller than the value measured earlier by us and by other groups on porous ice. In our earlier studies we had concluded that γ is independent of P_{HCl}, the reason being that we did not have enough sensitivity at that time to measure γ at sufficiently low P_{HCl} values.

We have also conducted experiments on porous ice, that is ice deposited from the vapor phase. The trend we observe is that as the vapor deposition rate and film thickness increase, the reaction probability γ for the $ClONO_2$+HCl reaction increases, approaching the values found in the literature. Leu *et al.* [1997] found a direct correlation between the vapor deposition rate and film thickness and the surface roughness of ice deposited from the vapor phase; our results for γ are consistent with this trend.

3. THEORETICAL STUDIES OF THE INTERACTION OF HCl WITH 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 appeared in the following publications:

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, *J. Chem. Phys.*, 113, 10,733-10,743, 2000.

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, *J. Phys. Chem. A*, 105, 7037-7046, 2001.

4. THEORETICAL STUDY OF THE INTERACTION OF HCl WITH NAT

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 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.

This work has appeared in the following publication:

Theoretical study of the interaction of HCl with crystalline NAT, Yves A. Mantz, Franz M. Geiger, Luisa T. Molina, Mario J. Molina and Bernhardt L. Trout, *J. Phys. Chem. A*, 106, 6972-6981, 2002.

5. RADICAL QUANTUM YIELDS FROM THE PHOTOLYSIS OF FORMALDEHYDE

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 (± 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 appeared in the following publication:

Measurement of Radical Quantum Yields from Formaldehyde Photolysis between 269 and 339 nm, Geoffrey D. Smith, Luisa T. Molina and Mario J. Molina, *J. Phys. Chem. A,* 106, 1233-1240, 2002.

6. EFFECT OF WATER VAPOR ON THE SELF-REACTION OF HO_2 RADICALS

We have investigated the effect of water vapor on the rate of the gas-phase self-reaction of HO_2 under atmospherically relevant conditions of temperature, pressure and humidity.

$$HO_2(g) + HO_2(g) + H_2O(g) \rightarrow HOOH(g) + O_2(g) + H_2O(g)$$

The experimental method employed consisted of a temperature controlled turbulent flow tube running between 100 and 300 Torr, coupled to a chemical ionization mass spectrometer (CIMS) detection system. HO_2 was produced inside a moveable injector by the reaction of H atoms with O_2. The H atoms were produced by passing a flow of diluted H_2 through a microwave discharge.

Water vapor was produced using a heated water bubbler with a 100-liter capacity. This system was used to produce water vapor at concentrations up to 6×10^{17} molecule cm^{-3} (ca. 80% relative humidity at standard room temperature) under fast flow conditions.

The normal experiments consisted measuring a dry HO_2 decay profile after setting the temperature and pressure conditions. Subsequently, a wet (water vapor added) profile was recorded. Typical decay profiles are shown in figure 3. Figure 4 shows the results, expressed as rate constant ratios, wet to dry; for clarity, error bars not shown in this figure.

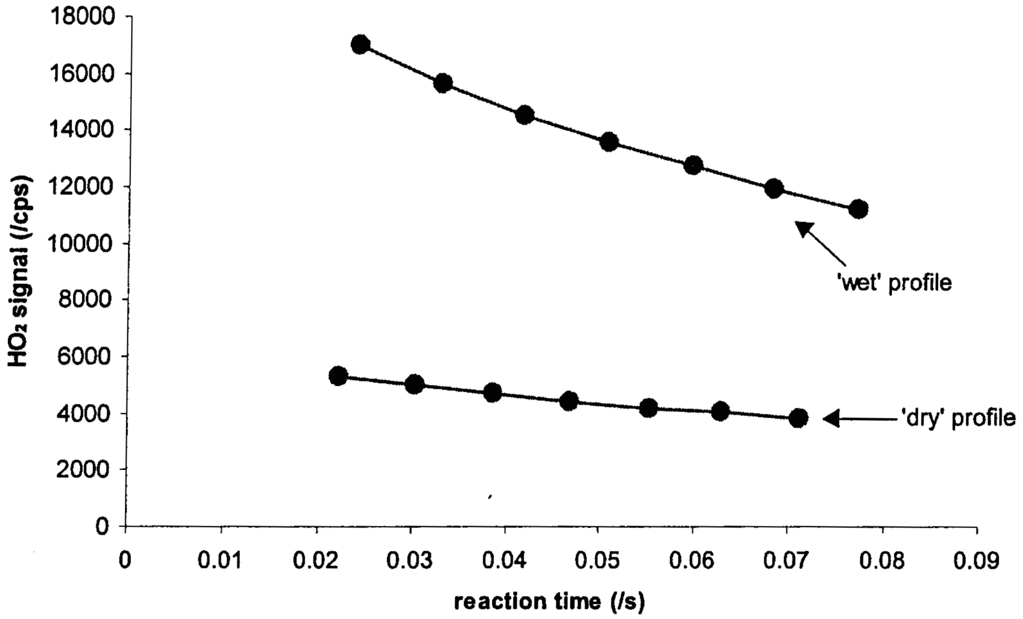

Fig. 3: Typical HO_2 decay profiles. Temperature = 10°C. Wet profile water concentration = 2.3 x 10^{16} molecule cm^{-3}. The profiles are offset due to the CIMS sensitivity towards water. The two profiles were compared and subsequent results were plotted on a relative scale following a correction for water in the CIMS system:

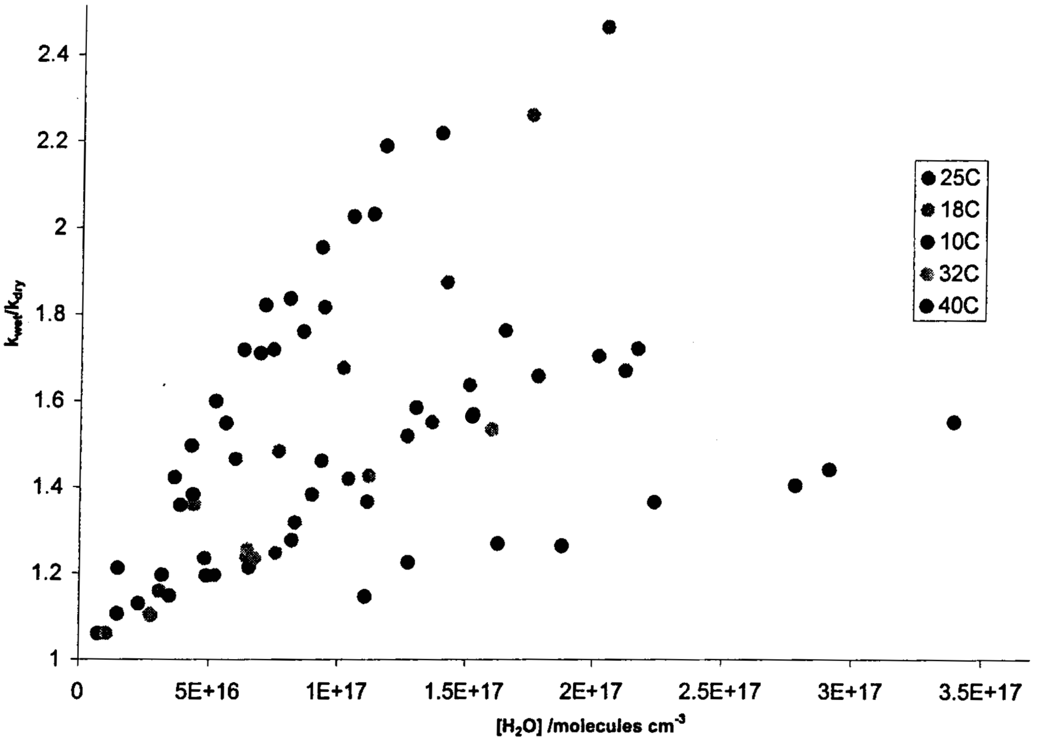

Fig. 4: Collected results showing the relative increase in the rate of the HO_2 gas-phase self-reaction upon addition of water vapor.

We observer that the addition of water vapor significantly increases the rate of the HO_2 self-reaction, and the effect and has a strong negative temperature dependence. In agreement with previous studies we found no pressure dependence for the water vapor effect.

A kinetics analysis produces the Arrhenius plot shown in figure 5.

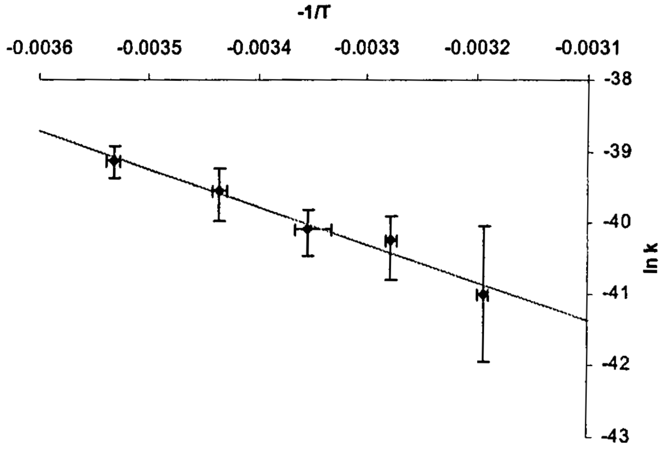

Fig.5. Arrhenius plot of the HO_2 self reaction.

The kinetics analysis yields the following expression:

$$k_{wet}/k_{dry} = 1 + 2.9\text{x}10^{-25}\,[H_2O]\; e^{(4900 \pm 1300\,/\,T)}$$

This result shows a significantly larger water vapor effect than the current NASA-Panel recommendation ($k_{wet}/k_{dry} = 1 + 1.4\text{x}10^{-21}\,[H_2O]e^{(2200/T)}$). This is especially true at lower temperatures; for example, at 10°C and 80% relative humidity this study suggests the rate of the HO_2 gas-phase self-reaction is increased by 3.5 times, in contrast with the NASA Panel recommendation factor of 1.8.

These results imply a large partitioning of HO_2 as the complex $HO_2{\bullet}H_2O$ in a cool moist atmosphere. Current models may be overestimating the atmospheric concentration of HO_2 and organic peroxides, and underestimating HOOH concentrations.

7. REFERENCES

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