

First Annual Progress report
For the Project

Laboratory Studies of Heterogeneous Chemical Processes of Atmospheric Importance

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LABORATORY STUDIES OF HETEROGENEOUS CHEMICAL PROCESSES OF ATMOSPHERIC IMPORTANCE

OBJECTIVE:

The objective of this study is to conduct measurements of chemical kinetics parameters for heterogeneous reactions of importance in the stratosphere and the troposphere. It involves the elucidation of the mechanism of the interaction of HCl vapor with ice surfaces, which is the first step in the heterogeneous chlorine activation processes, as well as the investigation of the atmospheric oxidation mechanism of soot particles emitted by biomass and fossil fuels. The techniques being employed include turbulent flow-chemical ionization mass spectrometry and optical ellipsometry, among others.

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.

ACCOMPLISHMENTS:

INTERACTION OF HCL WITH ICE SURFACES

Summary

The uptake of hydrogen chloride (HCl) on ice and ice-like particles is the first step in the chlorine activation process that leads to rapid ozone depletion in the polar stratosphere.^{1,2} A conventional model of physisorption of HCl onto an ordered ice surface³ cannot explain the experimental observation that HCl adsorbs to ice with high affinity^{4,5} and near-monolayer coverages^{5,6}, and that HCl is readily available on ice surfaces for rapid reaction with species such as chlorine nitrate^{2,4,5,7}. These observations are also unexpected given the low solubility of HCl in ice⁸⁻¹⁰ and the negligibly slow diffusion of HCl in bulk ice^{9,11}. We have proposed in the past that the uptake of HCl onto ice at stratospheric temperatures (-85 °C to -70°C) could induce the formation of a disordered region on the surface, or 'quasi-liquid layer' (QLL)³. The QLL is known to exist at temperatures near the melting point^{12,13} in pure ice, but its existence at stratospheric temperatures has not been confirmed¹⁴⁻¹⁸. We have studied the interaction of HCl with ice using the complementary approach of (1) high-sensitivity chemical ionization mass spectrometry (CIMS) detection to analyze the gas phase, and (2) phase-modulated ellipsometry to monitor the ice surface. Our results are the first to show that the presence of HCl indeed induces QLL formation under stratospheric conditions.

Experimental approach

The presence of a QLL was observed in our laboratory via ellipsometry on pure hexagonal ice down to approximately -30°C , in agreement with earlier reports. We also observed a change in signal consistent with QLL formation induced by the presence of concentrations of HCl at stratospheric levels in two different regions: $T > -35^{\circ}\text{C}$ and $T < -65^{\circ}\text{C}$. In the region $-35^{\circ}\text{C} > T > -65^{\circ}\text{C}$ we do not find any evidence of surface change upon exposure to approximately 10^{-7} Torr HCl. QLL formation was observed in the range of HCl partial pressures and temperatures in the vicinity of the solid-liquid equilibrium line on the HCl/ice bulk phase diagram. Our finding of two different regimes within the 'ice' region of the HCl/ice phase diagram is consistent with the findings of Hynes et al.¹⁹ who report that at 10^{-6} Torr of HCl the uptake probabilities α of HCl on ice drop from $\alpha > 0.1$ at 200 K (corresponding to our 'QLL' region) to $\alpha < 0.01$ upon increasing the temperature to above 205 K (corresponding to our 'non-QLL' region).

Ellipsometer signals and the corresponding CIMS signals were recorded under a variety of HCl partial pressures and temperatures. After exposure to HCl, surface change was observed after a time delay of 1-10 min, suggesting a secondary process occurring in the near-surface region. An aging effect was observed in that induction times were seen to decrease after the first exposure to HCl of an ice surface. Both the surface disordering and this aging effect were observed to be reversible. Assuming the optical constants for liquid water for this disordered surface layer, we estimate that the changes in the ellipsometry signal correspond to thicknesses of a few nm up to 100 nm depending on the quality of the ice-surface and the location in the phase-diagram. This is consistent with indirect estimates by Flückiger et al.²⁰ based on repetitive pulse Knudsen cell experimental results.

Additional evidence that HCl induces a physical change on the ice surface under stratospheric conditions comes from CIMS studies of the ice surface before and after exposure to HCl using CF_2CCl_2 (CFC-12) as an inert probe molecule. These measurements indicate that under conditions in which QLL formation was observed using ellipsometry, the total surface area available for CFC-12 adsorption decreases by 30% after exposure to HCl for both smooth and rough ice. The surface coverage of CFC-12 on a fresh smooth ice surface was measured to be 1.5×10^{15} molecule $\cdot\text{cm}^{-2}$, a value that is close to the predicted geometric surface area. The surface coverage of CFC-12 on a vapor-deposited ice surface was measured to be 2.4×10^{15} molecule $\cdot\text{cm}^{-2}$.

Uptake mechanism

The results of our CIMS studies of HCl adsorption on ice indicate two modes of adsorption on the ice surface. Upon the first exposure of a fresh ice surface to HCl, only a fraction of HCl is recovered upon desorption, indicating both reversible and irreversible adsorption processes. All subsequent exposures exhibit adsorption that is fully reversible

on the time scale of the experiment (minutes); on the other hand, saturation surface coverages vary with temperature. The uptake curves indicate HCl loss to the surface to be essentially constant for the second, third and fourth exposures. This effect was not observed to be reversible: after removing the HCl source for up to 1.5 hours, additional HCl desorption is not detected, and in the next uptake experiment no additional irreversible uptake is observed. The adsorption behavior is typical of an ice surface that has been previously exposed to HCl rather than a refreshed ice surface. These observations are in agreement with previous reports of a memory effect and irreversible loss in similar experiments.^{5,19,21}

At -77°C , the ratio of irreversibly to reversibly absorbed HCl molecules is 0.99:1. At -60°C , the ratio of irreversibly to reversibly absorbed HCl molecules decreases to 0.76:1. No dependence of this ratio on P_{HCl} was observed at any temperature. Saturation surface coverages were measured to be $2\text{-}3 \times 10^{14}$ molecule $\cdot\text{cm}^{-2}$ on smooth ice formed from the melt after the first HCl exposure, depending on temperature. Coverages for the first HCl exposure to a fresh ice surface were observed to be 1.5-2 times greater than aged ice surface coverages on smooth ice, depending on temperature. The ratio of irreversibly adsorbed HCl molecules to reversibly absorbed HCl molecules was not observed to be appreciably different for smooth ice films and rough ice films formed by deposition from the vapor phase. This indicates that increased density of dangling -OH groups at grain boundaries and surface defects is not the dominant source of strongly binding sites.

We interpret these two modes of adsorption as indicating the presence of two types of sites available for HCl absorption on ice crystals. The first binds HCl more strongly (type A) with a longer lifetime and the other (type B) binds HCl less strongly on the surface. We assume that the less strongly bound HCl is molecularly adsorbed, and the more strongly bound HCl could be bound via more than one hydrogen bond, perhaps to the point of being ionized.^{22,23} The rapid reaction of HCl with other chlorine reservoir species on ice surfaces suggests an ionic-type mechanism. There is no direct experimental evidence for HCl ionization on ice held at temperatures around 190 to 200 K.²⁴⁻³⁰ Computational studies show both molecular adsorption of HCl and ionization at ice surfaces; a literature survey has been provided elsewhere.²² A hint at the chemical nature of type A-bonded HCl comes from the surface coverages. We find the surface coverages to reach saturation above $10^{-7}\text{-}10^{-6}$ Torr of HCl whereas the coverages should be less than 0.001 ML under these conditions assuming molecular adsorption/desorption of a hydrogen-bonded HCl molecule^{31,32}. The observations can only be rationalized employing Arrhenius pre-exponential factors for the desorption that are 1000 times smaller than the typical pre-factor of $4 \times 10^{12} \text{ s}^{-1}$ at 200 K, as found by Isakson and Sitz²⁸ while freezing the barrier to desorption at 30 kJ/mol. Such low pre-factors typically arise when a pre-equilibrium has to be established beforehand, which could be recombination of ions in the present case. Therefore type A-bonded ice being an ionized form of HCl in H_2O is the most likely scenario.

If the ice surface is in equilibrium with its vapor phase, ~10-100 bilayers per second are adsorbed and desorbed at 185 K³³. It has been suggested that adsorbed HCl molecules could be buried by condensing water molecules to the extent that they are incorporated into the ice lattice, thus inducing disorder. Our results and those of previous studies by others¹⁶ suggest that this is not the case, and that HCl remains on the surface available for reaction. HCl adsorption onto an ice sample that was in equilibrium with water vapor and uptake onto a desorbing sample induced the same surface change in the ellipsometry experiments. In the CIMS uptake experiments, after removing the HCl source for up to 1.5 hours, no additional irreversible uptake was observed as would be expected if the adsorbed HCl molecules were being buried and 'fresh' adsorption sites were being created. This view is fully consistent with a picture of HCl being available in a near-surface region for reaction^{21,34}.

ATMOSPHERIC OXIDATION OF SOOT

Overview

Soot is an important and ubiquitous component of the troposphere with estimated global concentrations of 10^5 - 10^6 particles/cm³. Soot has potentially large effects on climate, both direct –through absorption of solar radiation– and indirect –through its effects on cloud particles.^{37,38} Soot reacts with photochemically-produced radicals and oxidants that can significantly change its physical and chemical properties, which include species such as O₃, NO_x, water vapor, HNO₃, H₂SO₄, and OH. Understanding these changes is necessary to determine the role of soot in cloud albedo and as cloud condensation nuclei (CCN), its residence time in the atmosphere as well as implications for its effects on human health. Little is known about the heterogeneous reactions mechanism for these processes and about the speed with which these reactions take place relative to gas phase reactions.

Water affinity (hydrophilicity) of soot

Freshly emitted soot is extremely hydrophobic, but through oxidation (ageing) in the atmosphere the surface becomes hydrophilic. Exposure to such species as O₃, OH, NO_x, H₂SO₄, and HNO₃ is expected to create polar functional groups on the soot surface that cause it to become more hydrophilic. The interaction of soot with water has important implications for its lifetime because of the nature of its removal mechanisms (washout and rainout).

Research in our laboratory confirms that exposure of soot to strongly oxidizing environments modifies its properties, activating it to the point of unconstrained water uptake under saturation conditions. We have employed four independent techniques to

probe the hydrophilicity of soot as a result of ageing: optical microscopy (OM), quartz crystal microbalance (QCM), environmental scanning electron microscopy (ESEM), and laser reflectometry (LR). A brief description of these techniques is given below.

Water adsorption isotherms obtained from QCM experiments are shown in Figure 1 for both fresh and aged soot. Aged (oxidized) soot exhibited enhanced hydrophilicity and reversible adsorption of water. Figure 2 shows ESEM and LR results, and as can be seen, ageing causes soot to activate at relative humidity levels relevant to the troposphere (indicated by the gray-shaded region in the figure). Activation relative humidities in the LR experiments are indicated by a sharp vertical rise in the measured signal. While freshly collected methane soot does not activate even at 15% supersaturation, soot exposed to HNO₃ vapor and OH/O₃/H₂O/UV activates at 1 ± 2 % supersaturation and 2 ± 2 % supersaturation, respectively. The individual panels in Figure 2 correspond to (a) plain glass slide, (b) glass slide treated with an organic silane to make it hydrophobic, (c) soot aged with exposure to concentrated HNO₃ vapor, (d) soot aged with exposure to OH/O₃/H₂O/UV, and (e) fresh soot. The dashed vertical lines labeled as (i), (ii), and (iii) depict the activation relative humidities detected for single soot particles using ESEM: (i) fresh soot, (ii) soot exposed to OH/O₃/H₂O/UV and (iii) soot exposed to concentrated HNO₃ vapor.

Description of experimental techniques

Optical Microscopy: Allows viewing of bulk condensation of water (activation) on the soot surface when it is exposed to varying levels of relative humidity by use of a flow cell.

QCM: Measures the change in oscillation frequency of a quartz crystal as mass is either deposited or removed from the crystal surface. Highly sensitive, it has a resolution of 0.5 Hz frequency, and thickness of 0.1 $\mu\text{g}/\text{cm}^2$.

ESEM: Allows 20 Torr water vapor to be retained within the chamber for imaging. The activation point is that at which bulk adsorption occurs on the soot surface as relative humidity is increased within the chamber.

Laser Reflectometry: Detection of the amount of light reflected from the sample surface when exposed to differing levels of relative humidity. A sharp increase in signal indicates condensation of water on the surface as the activation point.

We have conducted and completed experiments using the LR and ESEM techniques, while the optical microscopy measurements are in progress; the preliminary results support the LR and ESEM results.

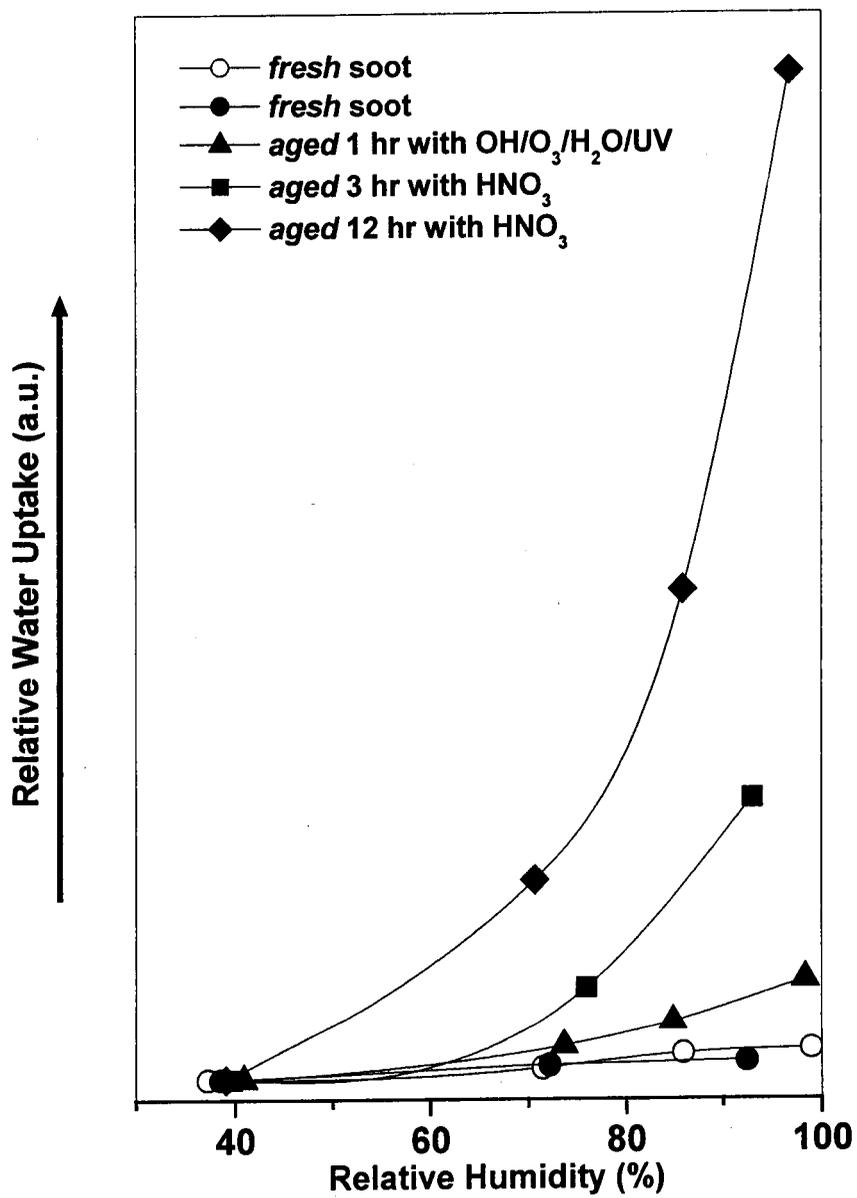


Figure 1. Water adsorption isotherms for methane soot determined with the quartz crystal microbalance.

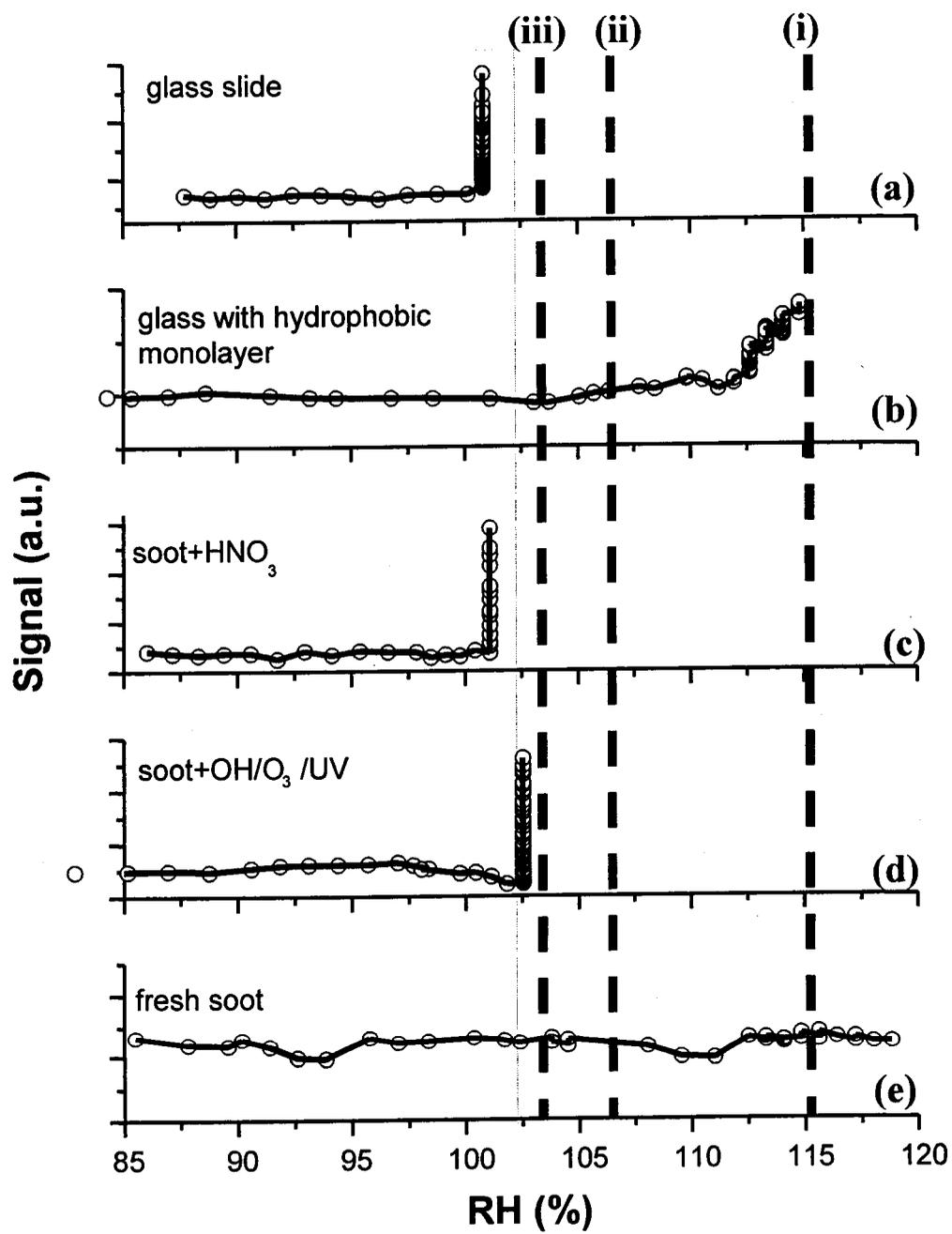


Figure 2. Water uptake of various samples at high relative humidity, determined with laser reflectometry.

Oxidation of soot initiated by reaction with OH

Reaction of OH radicals with soot is the initial step in the atmospheric oxidation of soot particles. Experiments conducted in our laboratory show that organic surfaces, serving as organic aerosol proxies, react very efficiently with OH radicals.³⁹ Furthermore, we have recently quantified the volatilization rate of alkane monolayers and of thin paraffin wax films induced by reaction with OH under low pressure conditions, thus leading to carbon loss from the particle. We are currently employing a quartz crystal microbalance coupled to a flow-tube apparatus fitted with chemical ionization mass spectrometry (CIMS) to examine the reaction between soot and OH at higher pressures, i.e. above 200 Torr, and in the presence and absence of oxygen. Whereas we have previously used the QCM technique to measure adsorption of water vapor on aged soot, here we anticipate a decrease in carbon mass for a fresh soot surface. The crystal's oscillating frequency is sensitive to changes in temperature, so that the generation of OH radicals must be carefully controlled. The temperature increase of the gas flow as a result of the microwave plasma is effectively controlled by means of a water circulation bath. As this is a real-time technique, we should see a frequency change of the QCM as the radicals attack the soot-coated crystal surface. The relative shift in frequency and time involved will be analyzed and compared to the results obtained under low-pressure conditions in order to unravel the reaction mechanism.

STATEMENT OF WORK FOR THE SECOND YEAR OF THE PROJECT:

1. The interaction of HCl vapor with ice will continue to be investigated experimentally using the ellipsometric and the flow-tube CIMS techniques, using a cylindrical ice tube made from ice single crystals with sizes in the several millimeter to centimeter range. The goal is to test the hypothesis that the irreversible component of the HCl uptake occurs at grain boundaries and triple joints, and to confirm the formation of the quasi-liquid layer on the large single crystals.
2. The CFC-12 surface coverage of large single crystal ice samples will be determined before and after exposure to HCl vapor, and the results will be compared to those obtained with porous and polycrystalline ice samples.
3. The carbon loss rate initiated by reaction of the OH radical with methane soot samples will be monitored with the quartz crystal microbalance as a function of oxygen pressure and relative humidity, to test the hypothesis that atmospheric oxidation of soot leads to the release of significant amounts of volatile organic compounds to the gas phase under realistic atmospheric conditions.

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