Investigation of the Reactive and Nonreactive Processes Involving ClONO$_2$ and HCl on Water and Nitric Acid Doped Ice

David R. Hanson* and A. R. Ravishankara*,†

*Aeronomy Laboratory, National Oceanic and Atmospheric Administration, 325 Broadway,
Boulder, Colorado 80303, and Cooperative Institute for Research in Environmental Sciences,
University of Colorado, Boulder, Colorado 80309 (Received: September 18, 1991;
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A flow tube reactor attached to a chemical ionization mass spectrometer was used to investigate the reactions of ClONO$_2$ with H$_2$O and HCl on pure water ice and nitric acid doped ice (referred to as NAT). The uptake coefficients, γ, for the above reactions were found to be nearly independent of the ice substrate thickness, suggesting that the geometrical surface areas of our ices are close to the true surface areas for such reactions. At low concentrations of HCl, close to those found in the atmosphere, its uptake due to physical adsorption was found to be very rapid, i.e., $\gamma > 0.3$; however it slowed considerably when a monolayer of HCl had been deposited on the surface. The surface of both water and NAT ice are shown to be saturated with HCl after the formation of a monolayer, suggesting that reactions involving HCl are confined to the surface. At high HCl concentrations the surface was altered by the formation of a hydrate or melting. The reaction of ClONO$_2$ with H$_2$O on pure ice was found to generate HOCl, which has an appreciable adsorptivity on the surface. The direct uptake of HOCl on water ice was observed and its adsorptivity was found to decrease at warmer temperatures. A direct reaction between HOCl and HCl to produce Cl$_2$ on both pure ice and a NAT surface was observed. It is proposed that the reaction of ClONO$_2$ with HCl on water ice can proceed through the formation of HOCl and its subsequent reaction with HCl to give Cl$_2$, while the reaction is direct on HNO$_3$-doped ice. The implication of these findings to the surface reactions in the atmosphere are discussed.

Introduction

There have been many recent laboratory studies of the conversion of ClONO$_2$ and N$_2$O$_5$ into more active forms of chlorine and HNO$_3$ through reaction with both HCl and H$_2$O on the surfaces of H$_2$O-ice and HNO$_3$/H$_2$O-ice.[1-8] These conversions, which do not take place in the pure gas phase but do on the particles, are believed to occur in the winter- and spring-time lower polar stratosphere. They are believed to be unique to the polar regions and are the first step in the polar ozone destruction phenomena.[9] Both H$_2$O-ice and HNO$_3$/H$_2$O-ice are present in the winter polar stratosphere,[10,11] and both types of materials have been found to efficiently facilitate most of these reactions.[1,2,4,7,8]

The hypothesis of the conversion of ClONO$_2$ to Cl$_2$ and to HOCl on ice surfaces in the presence and the absence of HCl is qualitatively supported by laboratory experiments and is consistent with atmospheric observations. However, the mechanisms, time scales, and possible bottlenecks in these conversions are unexplored. This lack of information limits our ability to quantify the rate and extent of the conversion processes in the polar stratosphere. Furthermore, it is difficult to extrapolate such processes to other situations, such as the tropical and midlatitude stratosphere or a perturbed stratosphere, for example, due to a large fleet of supersonic aircraft. In such situations the nature and availability of particulates could limit the conversion of the reservoir species ClONO$_2$ and HCl to active chlorine; the extent of the conversion would be of great concern. Also, there have been large discrepancies in the quantitative results on the above conversion processes. Determining the possible causes for such discrepancies would bolster our confidence in the application of these data to atmospheric calculations. For these reasons, we undertook the experiments described in this paper.

In a recent paper,[8] we described measurements of the ClONO$_2$ and N$_2$O$_5$ reaction probabilities, γ, on pure ice surfaces. We showed that a pure ice surface became contaminated with the nitric acid that is produced in these reactions, and a decrease in γ of a factor of 50 or more occurred after an amount of nitric acid approaching a monolayer had built up on the ice surface. This

contamination was responsible for the previously reported values[1,2,4] for γ(ClONO$_2$ + H$_2$O) being factors of 5-10 lower than our determination. The ice in the earlier experiments was quickly contaminated with HNO$_3$ because of the high concentrations of reactants that were employed. High reactant concentrations may affect the absorption/adsorption of HCl onto ice and NAT as well as the yields of HOCl and Cl$_2$ from the reactions of ClONO$_2$ with H$_2$O and HCl. Therefore, the influence of high reactant concentrations on the measured reaction probabilities is of major concern and this effect is explored further in this work.

The uncertainty in the actual surface area of the ice used to carry out the laboratory measurements introduces substantial uncertainty in the previously measured values of γ. The uncertainty in γ may be very large if the ice exhibits a "frosty" nature and the applicability of the γ determined in the laboratory to the atmosphere comes under question. In most of the previous laboratory experiments,[1-6,8] the ice was assumed to be perfectly smooth. Therefore, the geometrical surface area was assumed to be the surface area available for the uptake of gas-phase molecules. The actual ice surface available to the gas phase was not directly determined. In recent experiments performed over nitric acid-ices, Leu and co-workers[7,12] showed that the pores in their ice can greatly enhance the available surface area and thus contribute significantly to the loss of a gas-phase species. Using

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* To whom correspondence should be sent at NOAA.
† Also affiliated with the Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309.

a theory of porous catalysts,[12] they concluded that their substrates could have surface areas up to 10 times the geometric area of the flow tube wall! It is therefore necessary to test the assumption that thin water–ice surfaces prepared by depositing H_2O vapor on glass, such as those used by us, are closely approximated as smooth. These thin surfaces could have quite different properties than the HNO_3–ices studied by Leu and co-workers.[7,12] We present measurements of the reaction probabilities of N_2O_5 and $ClONO_2$ as a function of ice substrate thickness and show that possible pores or cracks in the ice do not significantly affect the measured uptake coefficients.

Knowledge of the adsorption behavior of HCl is important for understanding the heterogeneous reactions involving HCl. Previous studies of HCl "sticking coefficients" were performed at high [HCl], and the derived values are difficult to interpret. We present results from experiments conducted at [HCl] ranging from 10^9 to 10^{12} molecules cm^{-3}, the lower values being close to those found in the atmosphere. Monolayer HCl surface adsorption at low [HCl] and multilayer HCl hydrate formation at high [HCl] are both demonstrated.

The Cl-containing products of the reactions of $ClONO_2$ with H_2O and HCl, HOCl and Cl_2, respectively, have been identified in the previous experiments.[1,2,4,7] For the $ClONO_2$ + HCl reaction, the ice surfaces may have been more heavily doped with HCl than those found in the stratosphere, because of the high [HCl] employed, and thus exclusive production of Cl_2 needs to be shown at low reactant concentrations. We describe results from experiments conducted at low concentrations, [HCl] and [$ClONO_2$] < 10^{10} molecules cm^{-3}, that confirm the earlier results.

In the absence of HCl, the reaction of $ClONO_2$ with H_2O on ice produces HOCl and HNO_3. Molina et al.[1] noted the production of HOCl from the above reaction and observed that the HOCl product was retained by the ice surface, eluting after a time period of minutes in experiments conducted at 193 and 185 K. Leu,[4] in similar experiments performed at 200 K, also detected HOCl from the reactive uptake of $ClONO_2$ on ice; however, he observed no noticeable delay in the evolution of HOCl from the ice-coated flow tube. In addition, Tolbert et al.[3] noted production of Cl_2O as well as HOCl from the loss of $ClONO_2$ on ice. We have studied the loss of $ClONO_2$ on pure ice and HNO_3-treated ice to investigate evolution of the HOCl product and to determine if other molecules are also formed.

Finally, we have studied the reaction between HOCl and HCl on a pure ice and a NAT surface. We observed this reaction occurring in liquid sulfuric acid of 40 and 60 wt % H_2SO_4 and estimated its bimolecular rate coefficient.[13] In this work, using a clean, nitrate-free, gas-phase source for HOCl, we measured very high values for the reaction probability of HOCl on pure ice in the presence of HCl in the gas phase at concentrations of ~2 × 10^9 and 10^{10} molecules cm^{-3}. The implications of this finding to the mechanism of $ClONO_2$ reaction with HCl on ice and to the conversion of HCl to active chlorine in the atmosphere are discussed.

Experiment

All the experiments described here employed the same basic apparatus, a neutral flow tube, where the reactions (and other phenomena) of interest occur, and a detection system based on chemical ionization mass spectrometry. This apparatus is described by Hanson and Ravishankara,[8] and we present here only a brief summary.

The glass neutral flow tube, ~80 cm long, with an inner diameter of 1.89 cm was surrounded by a jacket, through which cooling fluid was circulated, and a vacuum jacket for thermal insulation. A double-walled injector was introduced at the top. Dilute mixtures of $ClONO_2$ or N_2O_5-in-He and HCl-in-He were flowed separately through this injector to vary the time (distance) for which the ice was exposed to these reactants. An insulated injector at the bottom of the flow tube was used to introduce an

H_2O/He mixture to form an ice layer on the inner wall of the flow tube. Approximately 1 mg of H_2O/cm^2 of glass was deposited over a 10–20-cm length of the flow tube to generate a ~10-μm-thick ice layer (assuming an ice density of 1 g cm^{-3}).

The temperature of the flow tube was maintained between 191 and 211 K. The temperature of the cooling fluid flowing through the inner jacket of the flow tube was monitored via two thermocouples at the entrance and exit to the cooling jacket; the substrate temperature was assumed to be that of the coolant. Pressure was monitored with a capacitance manometer located at the bottom of the flow tube. For high gas flow rates, the measured pressure was corrected (~10%) for the pressure drop across the measurement region of the flow tube. Carrier gas flow rates were measured with calibrated mass flow meters. The average carrier gas flow velocity in the neutral flow tube was between 1000 and 3000 cm s^{-1} and the pressure was ~0.5 Torr.

To avoid rapid evaporation of the ice substrate, water vapor was deposited at the top of the flow tube to saturate the He carrier gas before it entered the reaction zone. In spite of this precaution, there was still appreciable evaporation, especially at temperatures greater than 200 K, as the small He flow through the injector (typically 5% or less of the total carrier flow) was completely dry.

Reactants and products were detected using chemical ionization mass spectrometry, a versatile and sensitive detection technique which is described in detail elsewhere.[14a] Briefly, by choosing an appropriate reactant ion, the ion–molecule chemistry can be tailored for the sensitive and selective detection of the species of interest. The I^- ion was used to detect $ClONO_2$ and N_2O_5 as it does not react with any HNO_3 that may be present.[14b] The fluoride ion, F^-, was found here to react rapidly with HOCl to produce the ClO^- ion, and it is known[14c] to react rapidly with HCl to produce Cl^- and with $ClONO_2$ and HNO_3 to produce NO_3^-. SF_6^- reacts with HCl and Cl_2 to produce $F^-\cdot HCl$ and Cl_2^- ions, respectively.[14d] We also discovered that SF_6^- reacts with $ClONO_2$ to give an $F^-\cdot ClONO_2$ ion. Depending on the experimental needs, one of these reactant ions, I^-, F^-, or SF_6^-, was employed.

The $ClONO_2$ and N_2O_5 sources and the estimation of their concentrations were described in a previous paper.[8] The sample of $ClONO_2$ used here contained very little Cl_2 or Cl_2O and thus allowed accurate detection of the products. We estimated the initial concentrations of $ClONO_2$ and N_2O_5 by assuming that helium flowing through the cold trap containing the reactant was fully saturated with the reactant at its vapor pressure.[15] HCl was introduced from a 1% mixture of HCl-in-He, and its concentration was estimated from the known ion–molecule reaction rate coefficients. While the knowledge of the absolute concentration of the reactant is not required to obtain a reaction probability, estimating the fractional surface coverage requires such information.

Results and Discussion

Many of the measurements performed in the course of this work yield a reaction probability or uptake coefficient, γ. To obtain γ, the first-order wall loss rate coefficient was determined by measuring the relative loss of reactant as a function of exposure time to the substrate. γ was calculated from the first-order loss rate coefficients using the standard flow tube analysis techniques[16] and, when required, the more involved Brown[17] analysis which takes into consideration finite gas-diffusion rates.[18,19]

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(18) The diffusion coefficients from ref 8: $P[D_{R\cdot He}]$ = $A_R(T/200)^{1.76}$ Torr cm^2 s^{-1}, where A_{ClONO_2} = 176, $A_{N_2O_5}$ = 171, and A_{HCl} = 262 valid for the temperature range 180–220 K. We calculated the value for HCl as in ref 8, and it agrees with the values reported in ref 19.

For our experimental pressures and gas compositions, gas-phase diffusion of the reactant begins to significantly limit gas-phase transport to the substrate when $\gamma > 0.1$. For the case of $ClONO_2$-in-He at 200 K, increasing γ from 0.3 to 1 results in an increase in the measured first-order loss rate coefficient, k_m, of $\sim 20\%$. In other words, the measured value of k_m becomes insensitive to the value of γ. Still, the value of γ can be calculated by correcting for the diffusion limitation. However, since the values of the diffusion coefficients are not accurately known, accurate calculation of γ from k_m is not possible for $\gamma > 0.3$. Therefore we report γ as greater than 0.3 when the measured k_m is close to the diffusion limit.

Another important parameter for understanding these reactions is the approximate surface coverage by a molecule. In our experiments, the coverage was estimated by determining the number of molecules lost from the gas phase, to the surface, per unit surface area. The number of molecules lost was obtained by monitoring the absolute gas-phase concentration of the species while it was exposed to the surface, and the (initial) concentration when it was not exposed to the surface. The time integrated difference between the two concentrations, when multiplied by the volume flow rate, yields the total number of molecules lost. The mass spectrometer was previously calibrated for the detection of each of the species studied, to an accuracy of $\pm 50\%$. Division of the number of molecules lost by the surface area yields the surface coverage. For this calculation we assumed that the total surface area of the ice was that of the geometric area of the cylindrical flow tube.

The nitric acid doped ice was prepared by exposing a water ice substrate to HNO_3, $ClONO_2$, or N_2O_5. This exposure leads to a surface layer of ice that has HNO_3 in it. As discussed in our earlier paper,[8] we believe that this layer has the composition of nitric acid trihydrate (NAT) ice and behaves as NAT. For ease of presentation, this type of ice is referred to as NAT in the rest of this paper.

A large number of experiments aimed at determining different chemical and physical parameters were performed in the course of this work. For ease of presentation, further details of each experimental procedure are presented along with the discussion of the results.

(a) γ vs Substrate Thickness. Leu et al.[12] and Keyser et al.[12] demonstrated that the measured γ should increase as ice thickness increases if the substrate is porous and presented an equation to account for the increase assuming that the density and porosity of the ice are unchanged with thickness. The effect of pores or cracks in the ice, if present, is to increase the effective surface area of the ice for γ that are much less than 1. The reaction probability of N_2O_5 we measured on a pure ice surface, $\gamma_0(N_2O_5)$, is ~ 0.02. Therefore, our measured $\gamma_0(N_2O_5)$ should vary with thickness if our ice is porous. Also the uptake coefficients we measured for N_2O_5 and $ClONO_2$ on HNO_3-treated ice surfaces, which we denote by $\gamma_s(N_2O_5)$ and $\gamma_s(ClONO_2)$, are <0.01. Again, these uptake coefficients should vary with thickness if the pores in the ice contribute greatly to the measured γ. To check for the effect of thickness on γ, we investigated all three uptake coefficients as a function of thickness along with the uptake coefficient for $ClONO_2$ on pure ice, which is very large and is not expected to be thickness dependent in this model. We calculated the thickness of the substrate assuming its density to be 1 g cm^{-3}. This assumption is unlikely to introduce a very large error in the relative thickness of our substrate as the density is unlikely to change drastically with thickness in our experiments.

These experiments were performed as follows: An ice layer of a given thickness was deposited in 1–20 min. The reactant was introduced through the injector and allowed to condition the inside of the injector and the flow tube downstream of the ice deposit for approximately 10 min. This step was particularly important for N_2O_5 to ensure that all water in the injector and the bottom of the flow tube was removed via formation of HNO_3 which was pumped away. A measurement of γ_0 was performed as rapidly

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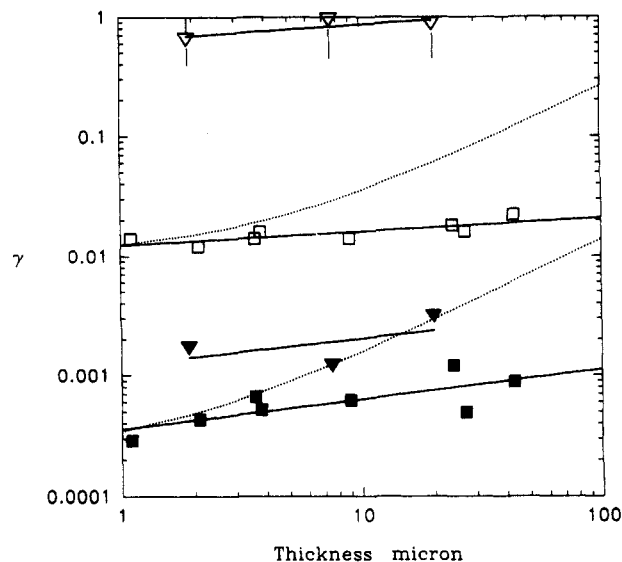
Figure 1. Measured uptake coefficients plotted against thickness of the ice coating. Results for N_2O_5 are squares and $ClONO_2$ are triangles. The open symbols are uptake coefficients over pure ice, and the filled symbols are uptake coefficients over HNO_3-treated ice. The solid line is a linear least-squares fit of ln γ vs ln (thickness) data to a straight line. The dashed line is the dependence expected from the model of Keyser et al.[12] for the effects due to porosity.

as possible to minimize the "poisoning" of the ice surface with HNO_3. Then, the injector was pulled back 10 cm to expose the entire ice surface to the reactant and the surface was allowed to "saturate" for 30–40 min, whereupon γ_s was measured. The absolute reactant concentrations were monitored throughout this "saturation" time to calculate the number of reactant molecules taken up. The majority of the uptake onto the ice surface occurred in the first few minutes of exposure.

Figure 1 is a plot of the reaction probabilities versus substrate thickness measured at 191 $\pm$ 1 K. The N_2O_5 results are plotted as squares, and those for $ClONO_2$ are plotted as triangles. The open points are reaction probabilities over fresh ice surfaces, γ_0, and the filled points are the reaction probabilities, γ_s, over the HNO_3-treated ice surfaces. As seen in Figure 1, both $\gamma_0(ClONO_2)$ and $\gamma_0(N_2O_5)$ are nearly independent of the thickness of the ice. The effects of the thickness on the measured uptake rate coefficients for both $ClONO_2$ and N_2O_5 were more noticeable on the HNO_3-coated ice than those on pure ice, although the dependencies were still small. If the situation described by Keyser et al.[12] is correct, the variation of $\gamma_s(N_2O_5)$ and $\gamma_0(N_2O_5)$ with thickness should follow the dotted lines. As mentioned above, the γ_s is expected, according to their theory, to be affected more by a "frosty" ice surface because the γ_s are much lower than γ_0; we used effectiveness factors of 0.6 and 0.2 for the cases of γ_s and γ_0, respectively, and a value of 10^4 cm^2 g^{-1} for the specific surface area of ice. It is clear that our measured values of γ_s do not follow the theoretical line predicted by Keyser et al.[12] The small increase in γ_s with thickness we observe may have been partly due to the inability to completely coat the ice with product HNO_3. Nonetheless, we conclude that the internal surface area of such ice deposits do not significantly affect the determination of γ when it is larger than 0.01. Furthermore, provided the γ_s measured here over substrates of a few micron thickness are correct, i.e., represent uptake measurements over an ideally smooth surface, our results suggest that the true values of γ near 10^{-3}–10^{-4} are factors of only 2–3 lower than the measured values over substrates that are 100 μm thick. Therefore, it is not necessary to correct the uptake coefficients, previously measured by us[8] as well as by the other previous workers,[1-6] for atmospheric applications.

There are several possible reasons why the treatment proposed by Keyser et al.[12] fails here. One is that they did not make the BET surface area measurements on the HNO_3-ice surfaces used for the uptake measurements: the BET measurements were performed on NAT samples prepared in a separate vessel. It is
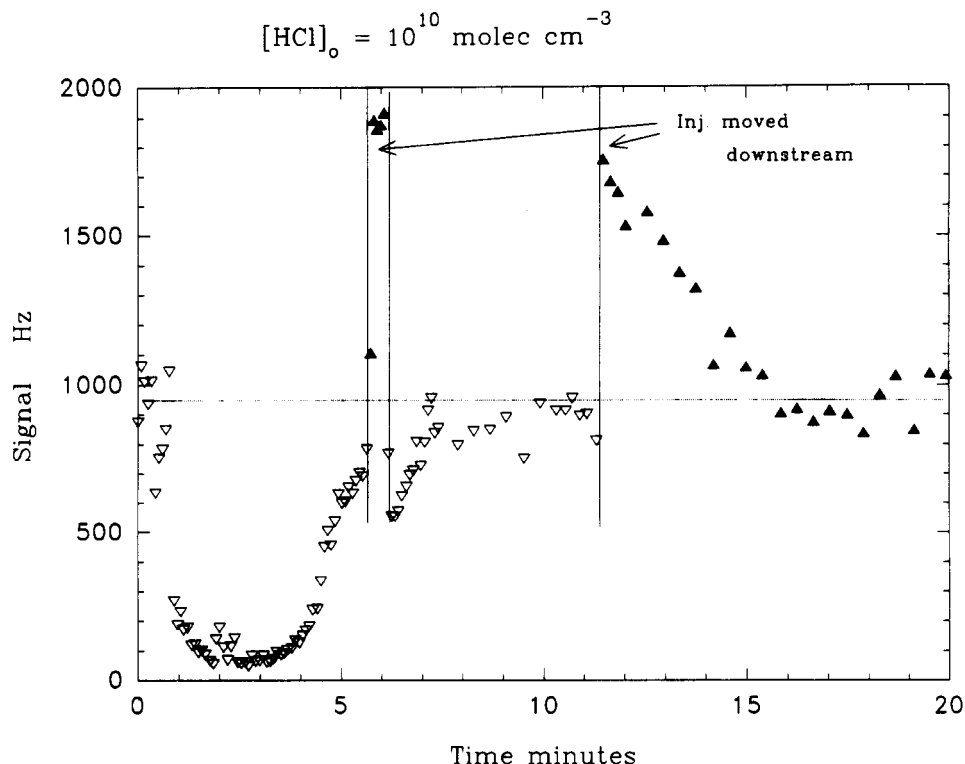
Figure 2. HCl concentration as a function of exposure time, for a 10-cm length of ice-coated flow tube. The exposure was initiated at 0.5 min, and the horizontal line indicates the unperturbed HCl signal. The filled triangles are the signal when the injector was moved downstream of the ice deposit, i.e., the ice was not exposed to HCl after previously being exposed to HCl. The vertical lines indicate when the injector was moved.

likely that the samples in the BET vessel were much thicker than the 50–100-μm layers deposited in the flow tube walls, and these surface area measurements may not be applicable to the thinner substrate that is actually present in the uptake measurements. Leu et al.[12] reported no effect on γ due to contamination of the surface with product HNO₃. As this has been shown to be a substantial problem,[8] especially at the high reactant concentrations used by these workers, it may have produced an artifact in their results and, at the very least, complicates their analysis.

Another possibility is that the nonpolar adsorbates such as N₂ and Ar used in the BET measurements diffused through the open structured ice and NAT substrate. If the diffusion is rapid, the BET method would have yielded a very high surface area. Stated a different way, the surface area measured using the small nonpolar adsorbates are inapplicable for the case of species such as ClONO₂, N₂O₅, and HNO₃.

In addition to γ we also determined the number of molecules lost per unit geometric area of the substrate as a function of its thickness. The measured N₂O₅ surface coverages on ice were unreliable due to variable HNO₃ impurity which was not monitored with sufficient precision to obtain surface coverage. ClONO₂ and HCl could be introduced into the flow tube with very little HNO₃ contamination, and the calculation of the surface coverage was much more reliable for these molecules.

The experiments with ClONO₂ and HCl (discussed below) revealed that approximately a factor of 2 more molecules per unit area were required to "saturate" the substrates when the thickness was increased from 2 to 20 μm. This indicates a larger surface available to the gas phase, which may be due to cracks or pores in the ice, or to increasing graininess of the ice surface at 20 μm. However, this value does not show a large increase as expected from the hypothesis of Leu et al.[12]

In the descriptions of the experiments that follow, we used ice substrates ~10 μm thick and assumed the ice surface was smooth. Its area was taken to be the geometric surface area of the glass flow tube wall.

(b) Physical Uptake of HCl by Ice. The uptake of HCl over pure and NAT ice was studied using experiments similar to that described in section a. After a pure ice layer was prepared, a mixture of HCl-in-He was added through the moveable injector.

The injector, whose tip was at the downstream end of the ice surface such that the ice was unexposed to HCl, was quickly pulled upstream exposing a 5–10-cm length of pure ice to HCl. Either the F⁻ or SF₆⁻ reactant ions were used to detect HCl.

Typical results for experiments with [HCl] at ~10¹⁰ molecules cm⁻³ are shown in Figure 2, as a plot of HCl signal vs time. For comparison, the horizontal line is drawn to indicate the initial HCl signal, [HCl]₀, i.e., the signal when HCl was not exposed to the ice surface. (The mass spectrometer sensitivity drifted slightly with time on occasion, and in this case the signal was normalized to the initial signal assuming that [HCl]₀ did not vary.) In the data shown in Figure 2, HCl exposure to the ice surface was initiated at about 0.5 min. The tip of the injector was briefly moved beyond the ice surface, at 6 min and again at 11.5 min. The data taken with the injector tip beyond the surface are represented as filled triangles. The initial HCl uptake coefficient over pure ice (i.e., at ~1 min in Figure 2) was determined to be ≥0.3.

It is clear from Figure 2 that HCl is taken up by a pure ice surface very rapidly with a high adsorption/absorption accommodation coefficient. The experimental uptake coefficient remains constant for a short period (~3 min at 1 × 10¹⁰ molecules cm⁻³ in Figure 2) and then decreases to a value <0.01. This value of the uptake coefficient is referred to as γ_s. For the case shown in Figure 2, γ_s was estimated assuming that the difference between the horizontal line and HCl signal at 10 min to be due to uptake on the saturated surface. It was not possible to determine this value accurately because of the desorption of HCl from the previously exposed ice when the injector was moved downstream of that part. The decrease in γ to 0.01 or less indicates that the surface (and/or the bulk of the substrate) was saturated with HCl. The decrease in γ with exposure time suggests that HCl is not being chemically converted to another form very rapidly. If it was being converted, to some extent, the converted form, say Cl⁻ or HCl·(H₂O)ₙ, must have been in equilibrium with the HCl form for it to escape from the surface. This assumption of physical dissolution is further substantiated by the observed changes in HCl concentration when the injector is moved downstream to stop exposure of HCl to the surface. Then, the concentration of HCl increases *beyond* what was being added from the injector! This

increase is due to the desorption of HCl from the HCl saturated ice. In addition to this physical adsorption, there appears to be a component of the loss which appears to be irreversible; this observation is discussed below.

The HCl uptake coefficient decreased considerably after a period of minutes, as pointed out earlier and shown in Figure 2. Knowing the initial concentration of HCl, $[HCl]_0$, we calculate the total number of HCl molecules taken up by the ice surface to be $\sim 5 \times 10^{14}$ molecules cm^{-2} for the data shown in Figure 2. We repeated such measurements with $[HCl]_0$ varying from 2×10^9 to 7×10^{10} molecules cm^{-3}. The number of HCl molecules taken up was $(5 \pm 1) \times 10^{14}$ molecules cm^{-2} independent of $[HCl]$ over this range; only the time for saturation changed. We also obtained the same surface coverage at 201 K for $[HCl]_0 \approx 1 \times 10^{10}$ molecules cm^{-3}. In one experiment, we varied the thickness of the ice from 3 to 30 μm and found the number of HCl molecules taken up by the ice surface to increase by a factor of 2. This small increase is similar to that observed in $ClONO_2$ experiments described above. We also performed an HCl uptake experiment over NAT ice at 191 K. The overall time behavior was the same as that over ice; however, the surface coverage at saturation was $(2-3) \times 10^{14}$ molecules cm^{-2}. This lower value could mean that the number of sites into/onto which HCl can be incorporated is smaller in NAT ice. However, the uptake of HCl on NAT ice is still large. HCl appears to be mostly physically adsorbed even on HNO_3-doped ice, thus the atmospheric NAT type particles should be able to retain a sufficient amount of HCl for reaction with $ClONO_2$ when they are exposed to atmospheric concentrations of gas phase HCl.

As seen in Figure 2, the number of molecules desorbing after the 11-min mark was not equal to the number of molecules adsorbing from the 1–6-min period. Furthermore, even if the ice surface was allowed to desorb for 5–30 min and then reexposed to HCl, the measured number of HCl molecules taken up was $\sim 2 \times 10^{14}$ molecules cm^{-2}, measurably smaller than that taken up by a fresh ice surface. These two observations indicate that the ice surface was altered upon exposure to HCl, and/or a fraction of the HCl that was taken up by the ice remained on the ice surface and did not desorb for 30 min. If the latter explanation is true, the HCl adsorption process we studied was not completely reversible.

The above experiment was not affected by a small amount of HCl that may dissolve into the bulk ice. The solid phase diffusion of HCl is so slow that essentially all HCl will be at the surface. The solubility limit of HCl in pure ice is 20 ppm.[20] Using the equation $d \approx (tD)^{1/2}$, where d is the thickness of bulk ice available to HCl, t is the ~ 1000-s exposure time, and D ($\sim 10^{-11}$ cm^2 s^{-1}) is the diffusion coefficient for HCl-in-ice, it can be shown that the layer of bulk ice into which HCl can diffuse, d, is ~ 1 μm thick. This layer may contain at most a tenth of the number of molecules at the surface.

When we used very high $[HCl]_0$ ($\sim 2 \times 10^{12}$ molecules cm^{-3}), there was unlimited uptake: $\sim 4 \times 10^{16}$ molecules cm^{-2} of HCl molecules were taken up with no sign of "saturation" on the time scale of several minutes. The results of this experiment are depicted in Figure 3 as plots of the logarithm of the HCl signal versus injector position. The measured HCl signals are shown as open symbols. The figure shows two different sets of data (open circles and triangles) taken about 6 min apart. It is clear that the measured HCl loss does not change with time. This time independent large HCl uptake can be interpreted as due to the growth of an HCl hydrate or possibly to the formation of a supercooled liquid on the surface of the ice. The concentration of HCl coming out of the flow tube while the entire ice surface was exposed to HCl was $\sim 3 \times 10^{11}$ molecules cm^{-3} at 191 K. At this temperature, the HCl hexahydrate is stable for HCl pressures $> 10^{-6}$ Torr (a concentration $> 5 \times 10^{10}$ molecules cm^{-3}) while the supercooled HCl/H_2O liquid (metastable) could arise for HCl pressures $> 3 \times 10^{-6}$ Torr (1.5×10^{11} molecules cm^{-3}).[20] The vapor pressure of H_2O ice at this temperature, 2×10^{-4} Torr,

(20) Hanson, D. R.; Mauersberger, K. *J. Phys. Chem.* **1990**, *94*, 4700.
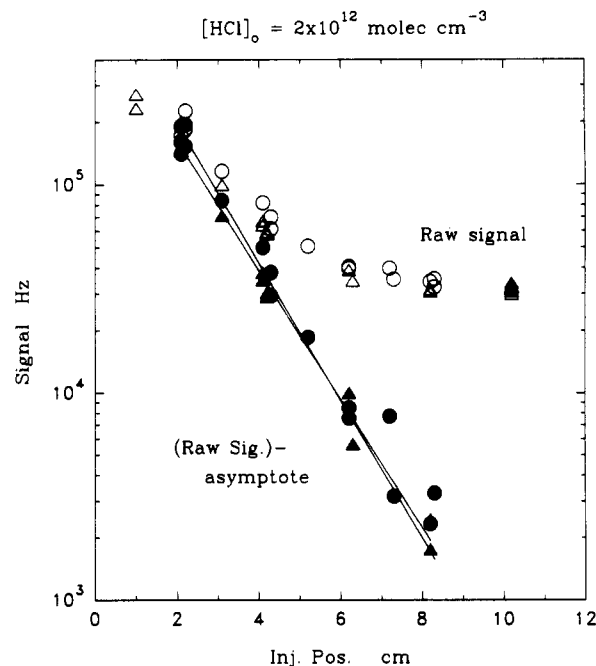
Figure 3. Uptake of HCl by an ice surface plotted as HCl signal vs injector position, when a large concentration of HCl was used. The open symbols are the data, and the filled symbols are [data – $data_{10cm}$], where $data_{10cm}$ was taken to be the asymptotic value (see text.)

which governs the concentration of H_2O in the gas phase available for growth of a hexahydrate phase, was sufficient for formation of such a phase. Alternatively, if a supercooled HCl/H_2O liquid was formed, the large uptake could be sustained because of the faster liquid-phase diffusion of HCl.

The constant HCl concentration eluting from the tube at an injector position of 10 cm can be viewed as the asymptotic value. Hence a plot of ln $([HCl]_x - [HCl]_{10cm})$ versus injector position should be linear, which is indeed true as shown by the filled points in the figure. The slope of such a plot is the first-order loss for HCl in forming the new phase on ice. The slopes of the lines, determined from a linear regression analysis, are shown as solid lines. These first-order loss rate coefficients lead to an accommodation coefficient > 0.3 for HCl onto this new phase. (At high reactant concentrations, the sensitivity of the current CIMS detection scheme decreases, i.e., becomes slightly nonlinear. Correcting for such a decrease in sensitivity at high concentrations would *increase* the slopes of the lines in Figure 3, and consequently the measured k_m and the calculated γ for this process.)

(c) Production of HOCl from the Loss of Chlorine Nitrate on Ice. We have shown the γ for $ClONO_2$ on pure ice to be high, on the order of 0.3 and possibly as high as 1.[8] Here we describe experiments aimed at identifying the products of reactive $ClONO_2$ uptake on ice. The product that leaves the ice was identified to be HOCl. Therefore, the other product is HNO_3, and it is left behind on the surface.

A freshly prepared ice surface at temperatures of 191–211 K was used for each measurement, and the initial $[ClONO_2]$ was maintained between 4×10^9 and 7×10^{10} molecules cm^{-3}. HOCl was detected via its reaction with F^- to give ClO^-. The concentration of HOCl and time rate of its evolution were monitored. Figure 4 shows the signals due to $ClONO_2$ and HOCl during this experiment. The signals for $ClONO_2$, along with a small contribution from HNO_3 (solid circles), and HOCl (open circles) are shown as a function of time. From 0 to 11 s, the ice surface was not exposed to $ClONO_2$. The small amount of HOCl shown in the figure for this time was produced either inside the injector or the lower part of the flow tube. At ~ 11 s, a 10-cm length of ice-coated flow tube was exposed to $ClONO_2$. As seen in the figure, the concentration of $ClONO_2$ drops sharply to a very small value. The rise in HOCl, however, has a noticeable delay of 10–15 s. At 25 s, the injector was moved back downstream of the ice to stop the exposure and the $ClONO_2$ signal increases instantly
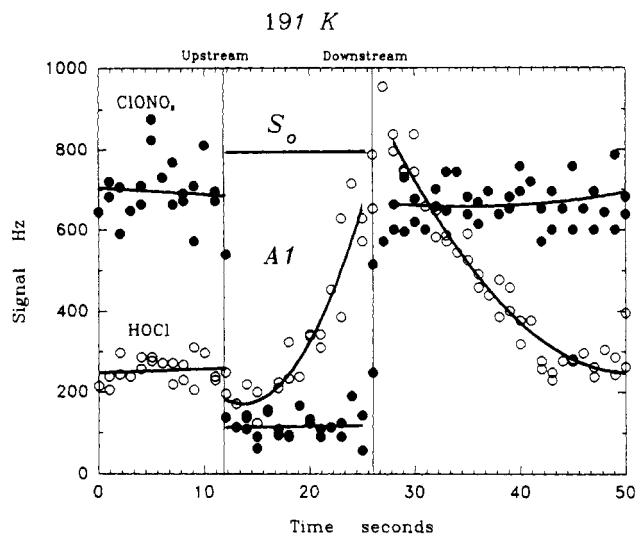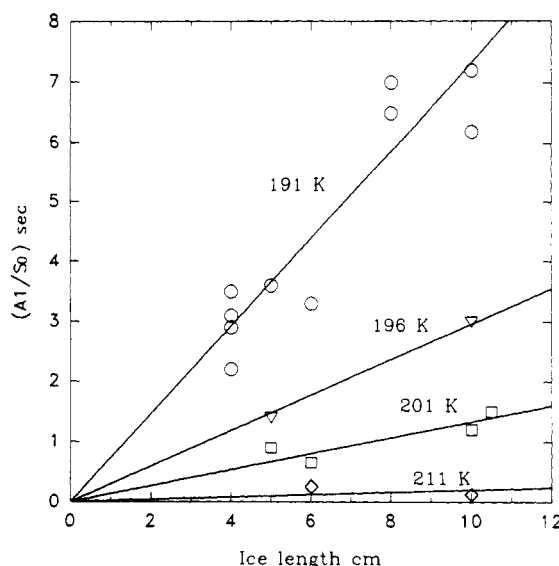
Figure 4. Evolution of product HOCl, open circles, from the loss of reactant ClONO2, filled circles, over a pure ice surface at 191 K. The vertical lines indicate when the injector was moved to initiate ClONO2 loss on ice and then to stop the ClONO2 exposure to ice. S_0 represents the final concentration of HOCl, i.e., when it has saturated the surface, and equal to the initial concentration of ClONO2. A_1 is the area between the solid line for HOCl in the middle panel and S_0.

Figure 5. Quantity $(A1/S_0)$, which is a relative measure of the number of HOCl molecules taken up by the surface (see text), plotted against length of ice exposed at the different temperatures indicated. The lines in the figure are linear regressions to the data and were forced through zero.

to its original value. However, the HOCl signal again has a noticeable delay in returning to its original value.

In all of our measurements of this type, and as displayed in Figure 4, the maximum signal due to HOCl was always comparable to the initial signal due to ClONO2. The relative detection sensitivity of the CIMS system to these molecules is approximately the same. The sensitivity is largely determined by the ion–molecule reaction rate coefficients and to a lesser extent by the transmission of the mass spectrometer to the product ions. Exothermic proton transfer reactions of the type $F^- + H-X \rightarrow HF + X^-$ are generally quite fast, on the order of 10^{-9} cm^3 s^{-1}.[14c] The rate coefficient for the F^- reaction with ClONO2 is $\sim 10^{-9}$ cm^3 molecule^{-1} s^{-1} as well;[8] therefore, the sensitivity for detection of HOCl and ClONO2 is, within a factor of 2, the same. These yield measurements are consistent with the ClONO2 molecule reacting with H2O on the ice surface yielding one HOCl molecule. We could not accurately quantify the yield of HOCl because of difficulties in calibrating our system for HOCl. However, we can confidently place a lower limit of 50% for the yield of HOCl.

Tolbert et al.[2] observed the production of Cl2O in the surface reaction of ClONO2 with H2O. Therefore, attempts were made to observe Cl2O evolution. Cl2O was detected via its reaction with F^-. The reaction of F^- with Cl2O has not been previously studied; thus, the rate coefficient and products of this reaction are unknown. Therefore, we first investigated the reaction of F^- with Cl2O. A known concentration of Cl2O, determined from its vapor pressure,[21] was introduced into the CIMS system and the decrease in the reactant F^- and increases in the product ion signals were measured. Cl$^-$ was identified to be the major product, with a small channel leading to ClO$^-$. (ClO$^-$ could also be a product of a secondary reaction.) A rate constant of $\sim 1 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} was determined using the standard procedure for the flowing afterglow system.[14a]

Using the measured rate coefficient for reaction of F^- with Cl2O, the possible production of Cl2O in our ClONO2 loss experiments was quantified. Both Cl$^-$ (from Cl2O) and ClO$^-$ (from HOCl with a minor contribution from Cl2O) were monitored upon exposure of ClONO2 to ice. Very little Cl$^-$ was observed. On the basis of the measured signals, we set an upper limit of $\sim 5\%$ for Cl2O production relative to HOCl. This observation suggests that either Cl2O is not produced in the reaction of ClONO2 with H2O or it stays in the ice once produced. Since it is very unlikely that the

solubility of Cl2O in ice is more than that of HOCl, any Cl2O produced would have been released into the gas phase. Therefore, we conclude that Cl2O is a minor product of the ClONO2 + H2O reaction. One possible reason for the observation of Cl2O by Tolbert et al. is that at the concentrations of ClONO2 used in their study, the concentration of the product HOCl was high, and HOCl could have reacted with itself to yield Cl2O.

We observed that HOCl, the product of the ClONO2 + H2O reaction, remained on the ice until the surface was saturated with HOCl. This observation points to adsorption of HOCl on ice rather than it being slowly formed via a reaction. This interpretation is substantiated by the experiment described in section e. Therefore, measurement of the extent of adsorption, i.e., fractional surface coverage as a function of temperature, would result in a determination of the heat of adsorption. Such experiments were carried out by varying the temperature of the ice and measuring a quantity that is proportional to the surface coverage. The results are given below.

Figure 4 shows the time evolution of HOCl upon exposure of ClONO2 to the ice. As pointed out earlier, the release of HOCl from the surface has a time lag, and at a certain time all the ClONO2 converted to HOCl came off the surface. One way to quantify the number of molecules of HOCl retained by the ice is to measure the area A1 marked in Figure 4. To account for fluctuations in the detection sensitivity of the CIMS apparatus, the relative surface coverage of HOCl was estimated by calculating the quantity $(A1/S_0)$, where S_0 is the maximum HOCl signal in that experiment (shown by a horizontal line in Figure 4). The measured value of $(A1/S_0)$ was essentially independent of the initial [ClONO2] (from 4×10^9 to 7×10^{10} molecules cm^{-3}) and hence [HOCl]. For the measurements at 191 K, the quantity $(A1/S_0)$ at the highest concentrations was $\sim 25\%$ smaller than that measured at the lowest concentration.

Figure 5 shows plots of $(A1/S_0)$ versus the length of exposed ice surface at four temperatures. For these experiments, approximately 10^{10} molecules cm^{-3} for [ClONO2]0, and thus [HOCl]0, were used. The equation for the Langmuir adsorption isotherm is $\Theta = b'(T)P/[1 + b'(T)P]$, where Θ is the fractional surface coverage, $b'(T)$ is the adsorption constant, T is temperature, and P is the partial pressure of the gas in atm.[22] This equation reduces to $\Theta \approx b'(T)P$ for low surface coverage. Thus,

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(21) Stull, D. R. *Ind. Eng. Chem.* **1947**, *39*, 540.

(22) Adamson, A. W.; Dormant, L. M.; Orem, M. *J. Colloid Interface Sci.* **1967**, *25*, 206. Orem, M.; Adamson, A. W. *J. Colloid Interface Sci.* **1969**, *31*, 278.
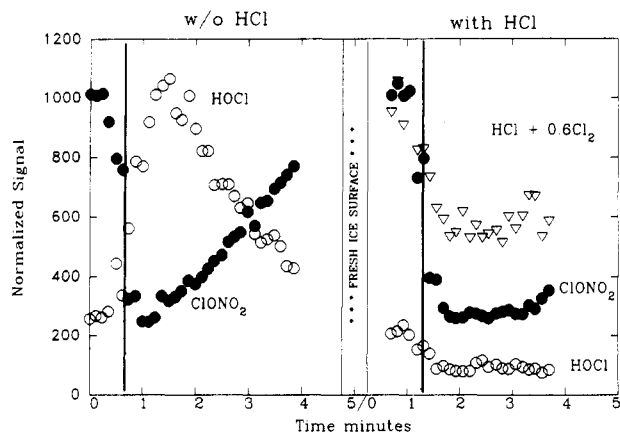
Figure 6. HOCl, ClONO₂, and HCl signals as a function of time for two different experiments conducted over pure ice. The first experiment (left panel) was ClONO₂ loss in the absence of HCl, and the second experiment (right panel) was ClONO₂ loss in the presence of a comparable concentration of HCl. The vertical lines represent when the ClONO₂ exposure to the ice was initiated. See text for further details.

the slopes of the lines, $y(T)$, in Figure 5 are proportional to Θ/P and therefore the adsorption constant $b'(T)$. [Note that in a normal Langmuir isotherm determination the surface area is held constant while the number of adsorbing molecules are varied.] Here, assuming that $\Theta \ll 1$ and that the free energy of adsorption, ΔG_{ads}, does not change with the fractional coverage, it can be shown that

$$\ln y(T) = (\text{constant} + \Delta S_{ads}/R) - (\Delta H_{ads}/RT)$$

where the constant relates the measured value of $y(T)$ with $b'(T)$ and is assumed to be independent of temperature. ΔS_{ads} and ΔH_{ads} are the entropy and enthalpy of adsorption and R is the gas constant. From such an analysis the value of ΔH_{ads} was found to be -14 ± 2 kcal mol⁻¹. By estimating the fractional coverage (assuming the geometrical surface area of the ice to be the real surface area), we obtain a value for $b'(T)$ and thus estimate ΔS_{ads} to be -40 ± 10 cal mol⁻¹ K⁻¹. The quoted errors in ΔS_{ads} and ΔH_{ads} are at the 2σ level and that for ΔS_{ads} includes the estimated error of a factor of 2 in the value of $b'(T)$ at 191 K, which was $\sim 10^7$ atm⁻¹. This large decrease in entropy is consistent with the loss of three degrees of translational freedom.[23]

The HOCl fractional surface coverage in all our experiments was much less than 1, i.e., 0.01 or less. It is possible that our assumption of ΔG_{ads} being independent of Θ is not strictly correct. Adamson and co-workers[22] have shown that ΔG_{ads} varied significantly near $\Theta \simeq 0.02$ in the case of n-hexane uptake on ice at ~ 250 K. Furthermore, as ClONO₂ is converted to HOCl, the surface is increasingly being deposited with HNO₃, the coproduct with HOCl in the reaction of ClONO₂ with H₂O. However, since the uptake of ClONO₂ is still what is expected over a fresh ice surface by the time HOCl has saturated the ice surface, we believe the surface to be mostly ice. In the absence of accurate knowledge of surface area, fractional coverage, and composition, our analysis is the best possible one.

Last, we noted that the presence of 5–10 cm of the flow tube covered with HNO₃-coated ice downstream of the pure ice surface did not affect the HOCl evolution. Therefore, HOCl was not noticeably adsorbed by such surfaces, even at 191 K, as well as not efficiently produced on them by the reaction of ClONO₂ with H₂O.[7,8]

(d) Reaction of ClONO₂ with HCl on Ice. In addition to the reaction with water, chlorine nitrate can also react with HCl. The enhanced uptake of ClONO₂ in the presence of HCl over NAT clearly points to such a reaction. The products of the reaction are believed to be HNO₃ and Cl₂. Since Cl₂ is very insoluble in

ice and NAT, it is expected to desorb. To investigate these processes, we repeated the measurements of ClONO₂ loss, but now in the presence of HCl at levels comparable to that of ClONO₂. Figure 6 shows the results for ClONO₂ loss over ice with and without HCl present. A fresh ice surface was prepared for each experiment, which were conducted at 191 K. The reactant concentrations were $\sim 10^{10}$ molecules cm⁻³. In the first experiment, shown on the left, production of HOCl correlates with the loss of ClONO₂, as noted earlier. As the ice becomes contaminated with HNO₃, the loss of ClONO₂ and the production of HOCl decreases. Note that the time scale for this contamination is much longer than for the release of HOCl noted in section c. In the second experiment, shown on the right, HCl was introduced over the ice simultaneously with ClONO₂ through a separate part of the injector. It is clear that HOCl was not released into the gas phase. (In fact, its signal decreases to the background level due to the absence of ClONO₂, which could have provided HOCl downstream of the measurement region.) Since both HCl and Cl₂ are detected as Cl⁻ in this experiment and because the rate coefficient for the reaction of F⁻ with Cl₂ is about a factor of 2 slower than that for F⁻ with HCl,[14e] there is a decrease in the Cl⁻ signal as HCl is lost and Cl₂ is produced.

Experiments such as the ones shown in Figure 6 were repeated with [HCl] as low as 2×10^9 molecules cm⁻³ and temperatures up to 201 K, being careful to maintain $[\text{HCl}]_0 > [\text{ClONO}_2]_0$. HOCl was not detected in any of these measurements, indicating that although the reaction probability of ClONO₂ with H₂O on ice is close to one, any HCl present leads to the generation of Cl₂. This change from HOCl production to Cl₂ generation in the presence of HCl may be due to a delay in the production of HOCl, i.e., the ClONO₂ molecule remains "intact" on the ice surface long enough for HCl to react with it, or, more likely, due to the reaction of HCl with HOCl that is produced. This possibility is explored further in the next section.
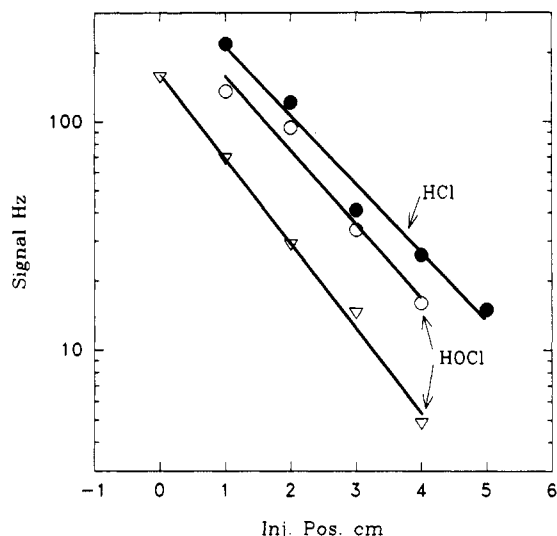
(e) Direct Observations of HOCl Uptake on Ice. In section c we described results of experiments which showed that HOCl formed by the reaction of ClONO₂ with H₂O was retained on the ice until it saturated. To investigate whether only HOCl produced at the surface is retained or if gas-phase HOCl can also be adsorbed, uptake of HOCl from the gas phase was directly measured. These measurements will also provide information on whether the reaction of ClONO₂ with H₂O is slow enough to cause a noticeable delay in the HOCl detection for the experiments in section c. HOCl was produced by passing HCl over Ca(ClO)₂ powder. This source worked best with the HCl flow turned off after initial exposure to Ca(ClO)₂. A small level of HOCl was produced that could be eluted for ~ 30 min after the HCl exposure. [Cl₂] was very high but decreased to only ~ 10 times [HOCl] when the HCl was turned off. We used $\sim 2 \times 10^9$ molecules cm⁻³ of HOCl for the uptake measurements.

The results of these HOCl adsorption experiments over a 6-cm length of ice-coated flow tube at 191 K was the same as that found for the HOCl produced by the ClONO₂ + H₂O reaction as shown in Figures 4 and 6. Because of the low levels of HOCl used here, the signals were rather poor. The results are shown in Figure 7. The relative fractional surface coverage obtained from the results shown in Figure 7 is similar to that for the 191 K data in Figure 6. Therefore, it appears that the delay in the HOCl evolution observed in the ClONO₂ uptake experiments is due to HOCl adsorption by the ice surface, as assumed in section c, and not due to a delay in the production of HOCl via the reaction of ClONO₂ with H₂O.

(f) Direct Observation of the Reaction of HOCl with HCl. At the end of section d we postulated that the production of Cl₂ from the ClONO₂ reaction with HCl on ice was due to the reaction of HOCl with HCl. Such a decomposition of the reaction scheme into elementary steps is of great importance for understanding the surface chemistry of ice and, more importantly, simplifies the heterogeneous chemistry of the stratosphere. Furthermore, such a reaction could be an important heterogeneous process in itself. Therefore, we investigated the reaction of HOCl with HCl directly. The source of HOCl was the reaction of HCl with Ca(ClO)₂
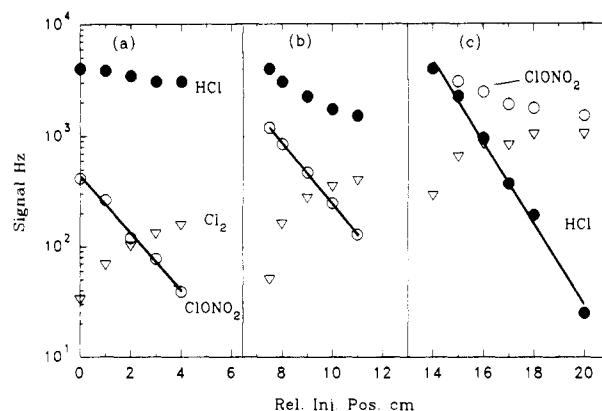
(23) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976; p 37.
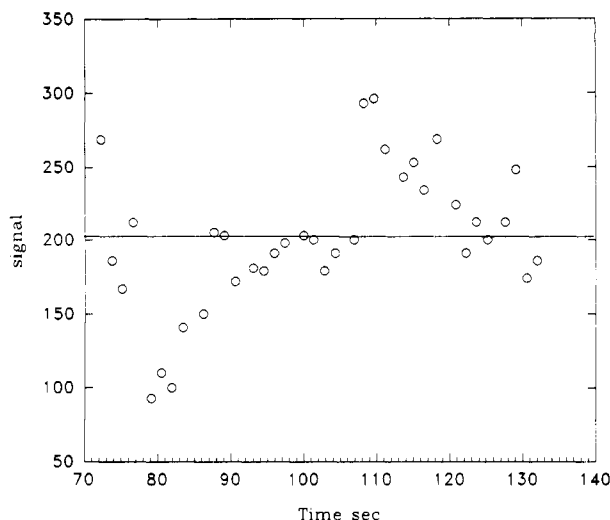
Figure 7. Concentration of HOCl as function of exposure time to a pure ice surface. The source of HOCl was HCl + $Ca(ClO)_2$. The injector was moved upstream at 76 s, initiating exposure of the ice surface, and then moved downstream at 108 s, stopping exposure. The horizontal line indicates the unperturbed HOCl signal, i.e., HOCl signal in the absence of exposure to ice.

Figure 9. HCl, $ClONO_2$, and Cl_2 signals as a function of injector position for three different [$ClONO_2$] over an HNO_3-treated ice surface. [HCl]$_0$ was $\sim 2 \times 10^{10}$ molecules cm^{-3} for all three experiments and [$ClONO_2$]$_0$ was (a) 6×10^9, (b) $\sim 1.5 \times 10^{10}$, and (c) 3×10^{10} molecules cm^{-3}. The three different situations are offset along the horizontal axis for clarity.

Figure 8. Loss of HOCl, open circles and triangles, and HCl, filled circles, as a function of injector position. The circles are for [HOCl]$_0$ and [HCl]$_0$ at 2×10^9 molecules cm^{-3}, and the triangles are the HOCl signal with [HCl]$_0$ increased by a factor of 10.

described above. The first-order loss of HOCl on ice in the presence of HCl at two different levels, $\sim 2 \times 10^{10}$ and 2×10^9 molecules cm^{-3}, was measured and found to be very large. Figure 8 shows the loss of HOCl (open circles) and HCl (closed circles) for [HCl]$_0$ at 2×10^9 molecules cm^{-3} and in a second experiment, HOCl loss (triangles) in the presence of 2×10^{10} molecules cm^{-3} HCl. Assuming a diffusion coefficient for HOCl-in-He of 220 Torr cm^2 s^{-1} at 200 K, i.e., between those of HCl and $ClONO_2$, the reaction probability of HOCl on ice in the presence of HCl was calculated to be >0.3 from the data shown in the figure. The uptake rate did not change with exposure time, and thus there were no saturation effects. This is to be expected if the products are Cl_2 and H_2O with Cl_2 desorbing rapidly.

The experiments involving the loss of $ClONO_2$ on ice in the presence of HCl showed that the reaction of HOCl with HCl yields Cl_2. To confirm this product, we measured the generation of Cl_2 from the direct reaction of HOCl with HCl on ice. The concentrations of HOCl and HCl were both approximately 2×10^9 molecules cm^{-3}. The generation of Cl_2 from this reaction was clearly seen above the Cl_2 background from the HOCl source. Within the error of our measurements, after correcting the measured signals for the relative sensitivities for detection of HCl

and Cl_2,[24] the concentration of Cl_2 produced was the same as that for HCl removed. This confirms that Cl_2 is indeed the product of the reaction of HCl with HOCl.

We previously observed a reaction between HOCl and HCl in/on sulfuric acid surfaces.[13] We estimated the rate coefficient to be $\sim 10^5$ M^{-1} s^{-1} and the Henry's law coefficient for HOCl in 40–60% acid solutions was estimated to be $\sim 10^4$ M atm^{-1} at 200 K. Now we have shown that HCl reacts with HOCl to form Cl_2 even on ice surfaces. On a sulfuric acid particle, the occurrence of this reaction could provide a mechanism for the conversion of HCl to an active form. The HOCl reactant could come from the gas phase or, to a lesser extent, made on the particle via the reaction of $ClONO_2$ with water. This mechanism could be particularly effective when the sulfuric acid aerosols are greatly enhanced due to perturbation such as a volcanic injection. Estimation of the contribution of such a mechanism to the generation of active chlorine requires better measurements of HOCl uptake on sulfuric acid aerosols. Similarly, the reaction of HOCl with HCl on ice or NAT particles could augment the conversion of HCl to active chlorine and could even be dominant when the $ClONO_2$ concentration is very low.

In one experiment, we prepared a NAT ice surface and observed the reaction of HOCl with HCl. HOCl in this case was introduced into the flow tube from an equilibrium mixture of HOCl, Cl_2O, and H_2O. With [HOCl]$_0$ and [HCl]$_0$ at $\sim 10^{10}$ molecules cm^{-3}, the reaction probability of HOCl was 0.1 ($\pm 25\%$) and Cl_2 was observed as a product. This value of γ is significantly lower than that observed over pure ice; however, it is still rather fast. Further investigations of this reaction on nitric acid/water solids are planned.

(g) Evolution of Cl_2 from $ClONO_2$ + HCl on NAT Surfaces. As mentioned earlier, the reaction of $ClONO_2$ with HCl on ice leads to the generation of Cl_2. This reaction, as shown above, may proceed via the formation of HOCl, which subsequently reacts with HCl to yield Cl_2. The loss of $ClONO_2$ on NAT surfaces, on the other hand, is not as well understood. The reactive uptake of $ClONO_2$ by NAT surface, in the absence of HCl, is much slower than that on ice. It is well established that the uptake of $ClONO_2$ on NAT in the presence of HCl is very rapid,[8] the same as that on ice with or without HCl present. Also, there is concern that the reaction of $ClONO_2$ with HCl could be slower at lower concentrations of HCl, such as those found in the atmosphere. To further investigate the reaction of HCl with $ClONO_2$, under concentration conditions approaching those in the atmosphere, the following series of experiments were carried out.

The evolution of Cl_2 from the reaction between $ClONO_2$ and

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(24) From ref 14d, the ratio of the overall ion–molecule rate coefficients is [F$^-$·HCl]/[Cl$_2$] $\sim$ 7. The production of F$^-$·HCl is only one of three channels however, and we found production of this ion had a branching ratio of $\sim 50\%$. Thus the relative detection sensitivity for HCl over Cl_2 is a factor of 3–4.

HCl on ice and NAT were measured. $ClONO_2$, HCl, and Cl_2 were simultaneously detected using the SF_6^- reactant ion. The ratio of $[ClONO_2]_0$ to $[HCl]_0$ was varied from 1/3 to 2. The uptakes of $ClONO_2$ and HCl were measured.

Figure 9 shows the signals due to $ClONO_2$, HCl, and Cl_2 versus injector position when $ClONO_2$ and HCl were simultaneously exposed to a nitric acid treated ice surface. Three different $[ClONO_2]_0$ were employed while the initial [HCl] was kept constant at $\sim 2 \times 10^{10}$ molecules cm^{-3}. The different decays, carried out over the same HNO_3-treated surface, are offset along the horizontal axis for clarity. In Figure 9a, the initial $[ClONO_2]$ was 6×10^9 molecules cm^{-3} and the observed first-order loss of $ClONO_2$ corresponds to a reaction probability >0.3. As seen in the figure, in spite of the noise in the signal, the concentration of HCl decreased by a third over the length of the substrate. The Cl_2 signal increases with injector position, in accord with the first-order loss of $ClONO_2$ and the subsequent production of Cl_2.

The decrease in the HCl concentration was equal to that of $ClONO_2$, which in turn was approximately the same as the increase in $[Cl_2]$.[24] This confirms that the stoichiometry of the overall reaction is $HCl + ClONO_2 \rightarrow Cl_2 + HNO_3$. Both the $ClONO_2$ loss and Cl_2 rise follow first-order kinetics. The first-order rate coefficient for the rise in Cl_2 is, within the uncertainty of the measurement, the same as that for the loss of $ClONO_2$. Therefore, the initial uptake of $ClONO_2$ must follow a first-order process and the subsequent reaction of $ClONO_2$ (on the surface or as the product of the $ClONO_2$ reaction with the surface) with HCl must be fast enough so as not to be the rate-determining step. As shown in section b, the physical uptake coefficient for HCl on both ice and NAT ice is very fast and hence is unlikely to be the bottleneck in the above experiments.

In the second series shown in Figure 9b, $[ClONO_2]_0$ was slightly less than but comparable to $[HCl]_0$; again both species are lost as the Cl_2 signal increases. The loss of $ClONO_2$ still follows a first-order rate law from which γ for $ClONO_2$ was calculated to be >0.3. Again the concentration of Cl_2 produced was the same as that of $ClONO_2$ lost.

Figure 9c shows the results when $ClONO_2$ was in excess over that of HCl. In this case, HCl displays a first-order wall loss rate coefficient that is $\sim 50\%$ greater than that of the $ClONO_2$ loss rate in Figure 9a,b. This larger loss rate coefficient is consistent with the $\sim 50\%$ larger diffusion coefficient for HCl-in-He than that for $ClONO_2$-in-He.[18] Even the rate coefficient for the rise in Cl_2 is larger and, within the precision of the measurements, the same as that for HCl loss. This is also consistent with the larger diffusion coefficient for HCl and the elution of Cl_2 being very rapid. In this case the amount of Cl_2 produced was again the same as the amount of HCl lost.

All these observations are consistent with the above mechanism of HCl reacting directly with $ClONO_2$ on the NAT surface. It does not enable us to separate the overall reaction into steps even if it was taking place in multiple steps.

It is conceivable that even on NAT, $ClONO_2$ reacts first with water to form HOCl and then HOCl reacts with HCl to form Cl_2. However, the observation that the uptake of $ClONO_2$ on NAT, without HCl present, is 2 orders of magnitude smaller than that in the presence of HCl, argues for a direct reaction between HCl and $ClONO_2$. In the atmosphere, the larger gas-phase diffusion coefficient and larger mean molecular speed of HCl than those of $ClONO_2$ would be sufficient to make the $ClONO_2$ uptake the rate-limiting step. Also, it is likely that HOCl is the product of $ClONO_2$ uptake on NAT. Under atmospheric concentrations, the HOCl would likely stay on NAT long enough for HCl to reach the surface and react with it. In any case, our experiments clearly show that for atmospheric concentrations the rates of reactions on the surface are not the rate-limiting steps in the conversion of $ClONO_2$ and HCl to Cl_2.

(h) Temperature Dependence of the Uptake Coefficient for $ClONO_2$ on HNO_3-Treated Ice. The uptake coefficient, γ, for $ClONO_2$ on pure ice is 2–3 orders of magnitude greater than that on HNO_3-treated ice or NAT. In both cases, $ClONO_2$ is reacting with H_2O to form HOCl. Therefore, the reason for the decrease

in γ on going from pure ice to NAT is the availability of water molecules that can react with $ClONO_2$, i.e., H_2O molecules in NAT are more tightly bound than in ice. To understand the hydrolysis of $ClONO_2$ by NAT, the temperature dependence of $ClONO_2$ uptake coefficient on HNO_3-treated ice was investigated. The procedure used was the same as that employed before. The temperature of the substrate was varied from 191 to 211 K.

The γ for $ClONO_2 + H_2O$ over HNO_3-treated ice clearly showed a distinct dependence on temperature. At 191 K, we measured a value of 2×10^{-3}, which is a factor of 3 lower than the 6×10^{-3} we reported earlier for 201 K.[8] The values of γ measured in the current study at 201 and 211 K were 4×10^{-3} and 8×10^{-3}, respectively. The present value for γ at 201 K is 33% lower than our previous value but overlaps with the previous value within the error bounds of the two measurements. We believe that the reproducibility of such measurements is on the order of 40%. The increase in γ_s with temperature is most likely due to the higher availability of water at higher temperatures.

Conclusions

We have demonstrated that the surface of ~ 10-μm thick layers of ice deposited on glass is smooth; thus our previous measurements of γ are not significantly affected by the "internal" surface area of ice and can be applied to the situation in the atmosphere.

The uptake of HCl onto both the ice and NAT surface is fast and leads to a surface coverage of between 2×10^{14} and 5×10^{14} molecules cm^{-2}, i.e., approximately a monolayer. The diffusion of HCl into the bulk of the ice is slow and is probably unimportant. Therefore, in the atmosphere, particles should already have HCl available for reactions. This simplifies the mechanisms of atmospheric conversion processes to one rate-limiting step, the uptake of $ClONO_2$, HOCl, or N_2O_5, as long as the concentration of HCl is not lower than those of $ClONO_2$, HOCl, or N_2O_5.

HOCl is produced stoichiometrically in the reaction of $ClONO_2$ with H_2O. Furthermore, HOCl is significantly adsorbed by pure ice surfaces at 191 K, much less so at higher temperatures. We were not able to detect HOCl adsorption onto NAT surfaces, even at 191 K, indicating a fractional surface coverage of HOCl on NAT of less than 10^{-3}.

We observed a direct reaction between HOCl and HCl on a pure ice surface with a reaction probability >0.3. Also, a preliminary value of ~ 0.1 was measured over a NAT surface for this reaction. In addition we detected the generation of Cl_2 in an amount equal to the HCl that was lost. This reaction could provide a new path for the conversion of HCl to active chlorine in the atmosphere.

We confirmed that the reaction of $ClONO_2 + HCl$ results in the formation of one Cl_2 molecule, over both pure ice and HNO_3-treated ice surfaces.

The reaction of $ClONO_2$ with HCl on pure ice may occur in two steps: $ClONO_2 + H_2O \rightarrow HOCl + HNO_3$ followed by $HOCl + HCl \rightarrow Cl_2 + HNO_3$. The latter reaction is fast enough to accommodate such a reaction scheme.

The direct reaction of $ClONO_2$ with HCl must also occur, in the case of NAT- or HNO_3-treated ices, as the $ClONO_2 + H_2O$ reaction is apparently too slow to account for the observed $ClONO_2$ uptake.

We observed a temperature dependence for the $ClONO_2$ uptake onto HNO_3-treated ice, without HCl present. The reaction $ClONO_2 + H_2O$ occurring on these types of surfaces is apparently limited by the availability of water. At higher temperatures we saw a higher uptake rate thus scaling with the available water vapor. Therefore, the efficiency of this reaction in the polar vortices would depend on temperature as well as the degree of dehydration.

The conversion of $ClONO_2$ and HCl to active chlorine occurs on the surfaces of the particles. For the surface reactions, therefore, it is more important to know the identity of the surface, i.e., is it ice, NAT, or other forms, than it is to know the bulk composition.

To sum up, $ClONO_2$ reacts very rapidly, either directly or as HOCl, with HCl in the polar stratosphere. Therefore the degree

to which the chlorine present as HCl becomes activated will be limited by the amount of $ClONO_2$ and HOCl present and, to a lesser extent, the amount of N_2O_5.[8] If the concentration of $ClONO_2$ gets too low to process HCl, the reaction of HOCl with HCl could help convert HCl to active chlorine. On the other hand, if HCl were used up, rapid activation of chlorine from $ClONO_2$ relies on the presence of pure ice surfaces, as HNO_3-treated surfaces (i.e., NAT) provide a much slower conversion of $ClONO_2$

to HOCl. In this case, the temperature and H_2O vapor availability could play important roles.

Continuous Wave Visible Laser Assisted Decomposition of Cr(CO)6 on a Growing Film: In Situ Observations

F. A. Houle* and **L. I. Yeh**[†]

IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099
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Direct measurements of volatile products desorbing from the surface of a growing film have been made by molecular beam mass spectrometry. Laser illumination of the substrate–film system induces two distinct regimes of decomposition of $Cr(CO)_6$ over a 300–950 K temperature range. The first of these is a pregrowth regime characterized by limited decomposition of the precursor, and the second is a growth regime in which near-total consumption of $Cr(CO)_6$ occurs. Both regimes are found at all temperatures. Each is characterized by complex, temperature-dependent chemistry which includes desorption of coordinatively unsaturated chromium carbonyl intermediates. CO ejection from the surface appears to involve several channels, including thermal and possibly electronically stimulated desorption. No evidence is found that recombinative desorption of C and O occurs, consistent with results of a separate study showing C and O concentrations in the films to be very low. The implications of these data for current ideas concerning the process of film growth from carbonyl precursors are discussed.

Introduction

Few experimental data exist concerning thermal decomposition mechanisms of the group VIb metal carbonyls at a surface, leading to film growth, a situation in stark contrast to that for the metal alkyls and the silanes.[1] Phenomelogical investigations of infrared[2] and visible[3-7] laser-induced deposition of tungsten films from $W(CO)_6$ for various applications have shown that if sufficiently high laser powers are used, the resistivity of the deposited metal is adequate for repair, masking, or restructuring. The requirement for high temperatures to obtain reasonable resistivities is consistent with results for blanket Mo and W films deposited by chemical vapor deposition (CVD).[8-10] A few analyses of films have been included in these studies, suggesting that high resistivities are associated with carbon and oxygen impurities, whose concentrations rise as deposition temperatures decline.[8,11] Systematic measurements of spatially resolved compositions of Cr, Mo, and W films deposited by focused visible laser light are consistent with trends found in the earlier work.[12,13] They show that CO from the parent carbonyl can be a significant contaminant and that it is largely dissociated to C and O in the film. The data have been used to obtain specific information on CO dissociation and desorption kinetics.[13]

Another significant observation in all laser-assisted thermal growth studies is the difficulty in nucleating a film. Long preillumination times (typically several seconds[6]) and rather high laser powers are often required for observable growth to commence, although the deposition rate is quite high once this stage has been passed. To address this problem, which limits practical applications, schemes such as depositing with high-power ultraviolet light, which would assist decomposition by photolysis,[14] or preilluminating by a low-power UV lamp to prepare nucleation sites[6] have been described. Measurements of deposition rates show that, once nucleated, the apparent activation energy for film growth is surprisingly low. Gas-phase pyrolysis experiments have

shown that the rupture of the first metal–CO bond is rate limiting for decomposition of Cr, Mo, W, and Fe carbonyls and that the bond energies are 2.0, 1.7, 1.9, and 1.7 eV, respectively.[15] It would be expected that the activation energy for film growth would be about the same if the surface chemistry resembled gas-phase decomposition. In fact, values of 1.0 and 0.8 eV were measured for Mo and W carbonyls in CVD,[8] 0.8 eV for W from infrared laser deposition,[2] and 0.4 eV for W and 0.7–1.0 eV for Mo in high-power UV laser deposition.[14] Since these rates include the much slower nucleation times, it is evident that decomposition steps leading to film growth are significantly more facile on the surface of the growing film than in the gas phase. Some aspects of this autocatalytic nature of film growth from the carbonyls were investigated in a study of electron beam induced nucleation followed by CVD using Cr and Fe carbonyls.[11] The apparent

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[†] Present address: Exxon Research and Engineering Co., Clinton Township, Route 22 East, Annandale, NJ 08801.