Uptake and Reaction of $ClONO_2$ on Water Ice and HCl Trihydrate at Low Temperatures

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Chlorine nitrate adsorption kinetics and uptake have been measured on ordered ice and HCl trihydrate films at temperatures below 150 K. Reaction was followed using a thermal molecular beam, with mass spectrometric detection of gas-phase products and temperature-programmed desorption (TPD) and IR to identify adsorbed species. The sticking probability (S) on pure water ice is (0.98 ± 0.03) at 85 K and remains near unity for temperatures up to 145 K. Initially S is independent of the $ClONO_2$ uptake, indicating a trapping mechanism for reaction. A molecular state which desorbs near 120 K during TPD is identified as a precursor state and above this temperature molecular $ClONO_2$ is not stable on the surface and adsorption forms HOCl and nitric acid hydrate. On a clean ice surface the reaction probability starts to decrease after 0.1 monolayer of $ClONO_2$ has adsorbed, reaction ceasing ($S < 5 \times 10^{-2}$) at an uptake of (0.25 ± 0.05) monolayer, independent of temperature. Reaction occurs even at low temperature, where the surface is immobile, indicating that $ClONO_2$ hydration can occur on the ice surface and does not require an extensive hydrate cage. The saturation stoichiometry is consistent with a surface covered with HOCl and an amorphous nitric acid trihydrate film. The initial reaction probability for $ClONO_2$ uptake onto pure HCl trihydrate films was similar, (0.98 ± 0.05) for temperatures between 85 and 145 K with some chlorine desorbing promptly into the gas phase even at 85 K. The uptake of $ClONO_2$ increases from 0.5 to ca. 1 monolayer above 125 K, the temperature at which HCl starts to transport into water ice films, reaction extending beyond the top layer of the HCl trihydrate surface.

1. Introduction

Heterogeneous reactions on the surface of polar stratospheric clouds (PSCs) are known to play a crucial role in the annual depletion of stratospheric ozone.[1,2] These PSCs are comprised of two general types. Type 1 PSCs consist of a mixture of HNO_3 and H_2O, in either a crystalline phase[3−5] (type 1a) or a liquid phase[6,7] (type 1b) and are formed at temperatures around 193 K under normal stratospheric conditions. Type II PSCs consist of crystalline water ice and are formed at temperatures at or below the stratospheric ice point of 188 K during the Antarctic mid winter. Of particular importance are reactions which convert inactive reservoir species $ClONO_2$ and HCl into photochemically active forms, such as Cl_2 and HOCl, as shown schematically in reactions 1−3,[1,2,8,9]

$$ClONO_2 + H_2O \rightarrow HOCl + HNO_3 \qquad (1)$$

$$HOCl + HCl \rightarrow Cl_2 + H_2O \qquad (2)$$

$$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3 \qquad (3)$$

Hanson[10] found that the reaction probability for $ClONO_2$ on a clean $H_2{}^{18}O$ ice film at 190 K was $\gamma > 0.1$ and showed that the Cl−ONO_2 bond was broken, consistent with nucleophilic attack of water on the Cl, concluding that neither ionization nor dissociation is a prerequisite for heterogeneous reaction of $ClONO_2$. Other experimental[11−13] and theoretical studies support nucleophilic attack on the chlorine atom as the mechanism for reaction.[14−17]

Above 155 K the HOCl produced from reaction 1 desorbs from the ice surface,[18] limiting the importance of reaction 2 as a source of Cl_2 under atmospheric conditions. However, at lower temperature HOCl remains adsorbed on the ice surface as a reaction product, probably bound as a proton donor to a surface water.[19,20] HNO_3 is strongly hydrated and remains adsorbed on the ice surface even at temperatures up to 200 K.[21] Experiments using FTIR reflection−absorption spectroscopy, conducted under ice frost point conditions at 185 K, suggest that the composition of the condensed nitric acid hydrate species is that of a supercooled liquid, with a composition slightly more dilute than (HNO_3:$3H_2O$)[21] while Hanson and Ravishankara have suggested the formation of nitric acid trihydrate (NAT) from flow tube measurements.[22] As the uptake of $ClONO_2$ proceeds the surface changes from pure, crystalline ice to an amorphous or crystalline hydrated nitric acid, depending on the temperature. It is clear that the rate of adsorption of chlorine nitrate on ice is very sensitive to the surface coverage of HNO_3,[18,22,23] but the kinetics of this process, and how they depend on $ClONO_2$ uptake and temperature, remain ill-defined.

Horn et al.[11] have suggested that the reaction mechanism depends on the availability of surface water and on the temperature of the ice. At a surface temperature of 140 K, and in the absence of a partial pressure of water, exposure to $ClONO_2$ initially leads to formation of HOCl and hydrated nitric acid bands, with molecular nitric acid bands forming at higher exposures. Molecular nitric acid will immediately solvate when excess water is available and its formation in the later stages of adsorption may be due either to the absence of free water or to a change in the mechanism for reaction. It was suggested that nucleophilic attack on the Cl atom was assisted by pre-ionization of $ClONO_2$ along the Cl−O bond during hydration.[11] Sodeau et al.[12] observed IR bands which were attributed to $[H_2OCl]^+$

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and nitrate ions as reaction products during reaction at 180 K, consistent with this mechanism,[13] although the assignment to $[H_2OCl]^+$ has been disputed.[15,24] Bianco and Hynes[15,24] have proposed that nucleophilic attack on the Cl is mediated by proton transfer to the ice lattice, proposing a cyclic transition state for $ClONO_2$ adsorbed on the ice I_h basal plane, with three hydrogen-bonded water molecules assisting concerted electron−proton transfer. Increasing the number of water molecules appears to reduce the barrier substantially,[14] while other calculations suggest that a significantly larger hydration shell is required to stabilize ionic products, $ClONO_2$ ionizing only when incorporated into a vacancy in the ice bilayer.[16,25]

During the reaction of $ClONO_2$ with HCl adsorbed at an ice surface (eq 3), Cl_2 is produced promptly in the gas phase[18,26] but no gas-phase HOCl is observed, whereas this is formed in the absence of HCl. This suggests that reaction takes place directly between hydrated Cl^- which is already present on the surface and a partially ionized precursor $Cl^{\partial+}ONO_2^{\partial-}$, rather than via an HOCl intermediate. Theoretical work also supports direct attack by hydrated Cl^- on $ClONO_2$ as the source of Cl_2.[17,27]

Experiments conducted under stratospheric temperature and water vapor conditions provide information on reaction rates and the production of gas-phase products relevant for numerical modeling. The initial reaction probability for reaction 1 on an ice surface is high at stratospheric temperatures,[22,28] with a value of $\gamma_1 = (0.2 \pm 0.05)$ quoted in the literature.[26] However a recent laser-induced thermal desorption (LITD) study at temperatures below 140 K yielded reaction probabilities of just 0.03, falling to less than 5×10^{-3} at 140 K.[29] Extrapolating these results to stratospheric temperatures, assuming a precursor mediated adsorption model, produced a reaction probability of 10^{-4}, much lower than the accepted literature value. It was suggested that this discrepancy might be caused either by the increased mobility of the ice surface or by water condensation enhancing the reaction probability at higher temperatures. This study also found that $ClONO_2$ hydration was inhibited at a nitric acid coverage of roughly 1 monolayer,[29] concluding that the reaction is limited to the surface or near surface region of ice at these low temperatures.[22] Measurements of the reaction probability for (eq 3) at stratospheric temperatures gave 0.14 and 0.26 at 200 and 180 K, respectively.[26,30]

Molecular beam adsorption experiments allow us to quantify the uptake of $ClONO_2$ onto pure and HCl-saturated ice surfaces, providing accurate probabilities and saturation coverages for reactions 1 and 3 at low temperature ($T \leq 145$ K). The reactions were followed by monitoring adsorption onto thin, well-defined crystalline ice I_h films, using an effusive molecular beam with mass spectrometric detection of the directly desorbed products and temperature-programmed desorption of the final ice surface. Absolute uptakes were obtained directly by calibrating the beam flux, allowing us to quantify the influence of the reaction products on adsorption and to determine the stoichiometry of the surface or bulk acid ice film produced. We show that $ClONO_2$ hydration is extremely efficient, occurring even at 100 K, but that reaction is strongly poisoned after adsorption of just 0.25 ML of $ClONO_2$. Adsorption occurs via a precursor-trapping mechanism, and a $ClONO_2$ precursor state is identified by TPD. Reaction with HCl occurs even at 85 K via a similar trapping mechanism, but the saturation uptake of $ClONO_2$ increases at temperatures above 120 K where transport in the HCl hydrate becomes sufficient to allow Cl^- from the first few layers to react.

2. Experimental Section

Reactive uptake of $ClONO_2$ was studied using a thermal molecular beam to expose thin layers of ice to $ClONO_2$. Experiments were conducted in a UHV chamber,[31] equipped with LEED, reflection−absorption IR spectroscopy (RAIRS), with a background pressure in the 10^{-10} mbar region. The ice layers were grown on a Pt(111) single-crystal substrate[32] which was cleaned by sputtering and annealing, the cleanliness being checked by LEED and thermal desorption. The metal substrate was mounted on two Ta heating wires attached to a liquid nitrogen cooled manipulator. This allowed the ice film to be maintained at a selected temperature, or heated to generate temperature-programmed desorption (TPD) spectra which were used to characterize the ice films and to identify reaction products. TPD spectra were obtained using a VG SX200 and a VG Smart IQ^+ quadrupole mass spectrometer at a heating rate of 1.4 K s^{-1}. This arrangement resulted in extremely clean TPD spectra, with no detectable background ($\Delta P < 10^{-11}$ Torr) being desorbed from the sample or supports when the clean Pt(111) sample was heated through the water and $ClONO_2$ desorption peaks.

Ice layers were formed by using the molecular beam to deposit H_2O onto the substrate at a controlled rate, typically 0.01 ML s^{-1}, with a background pressure of less than 2×10^{-10} Torr water in the chamber.[32] Crystalline hexagonal ice I_h was grown by depositing H_2O onto the Pt(111) crystal at a temperature of 138 K. The resulting ice films were characterized using a combination of RAIRS spectroscopy, LEED and TPD.[32] TPD spectra of the clean ice films grown in our chamber show no detectable trace of any other adsorbed species. RAIR spectra of the ice films were measured using a Mattson 6020 FTIR spectrometer with 4 cm^{-1} resolution. HCl-saturated ice films were made by dosing the crystalline ice films with a HCl beam at 137 K. Earlier work has shown that ice dosed with HCl under these conditions result in the formation of ice films with a saturation stoichiometry of ($HCl{:}3H_2O$).[33,34]

The molecular beam, which was used to deposit the water ice film and to dose HCl and $ClONO_2$, was formed using a glass nozzle beam source, operated in the molecular flow regime with a backing pressure of a few Torr. The beam was differentially pumped by two turbomolecular pumps and defined by a skimmer and a collimating tube to provide a spot 5 mm in diameter on the crystal substrate.[31] Relative beam intensities were calibrated by determining the flow rates of water and $ClONO_2$ through the nozzle. This allowed the flux of different species to be obtained directly from the backing pressure and converted to an absolute flux by reference to the H_2O uptake kinetics. Water TPD show a distinct desorption peak near 168 K for the first bilayer of water on Pt(111), followed by the growth of a multilayer peak at lower temperature.[31] In conjunction with sticking measurements this allowed the absolute flux of water in the molecular beam to be calibrated accurately as a function of the nozzle backing pressure. Uptake and reaction probabilities for $ClONO_2$ were measured using the direct reflection technique of King and Wells.[35] This technique provided sticking probabilities for $ClONO_2$ with an absolute accuracy of ca. ±0.03 and a lower limit of $S > 0.05$ which can be measured. $ClONO_2$ uptakes are quoted in monolayers (ML) relative to the water density of the ideal $(\sqrt{3} \times \sqrt{3})R30°$ bilayer on Pt(111) (1.1×10^{15} molecules cm^{-2}).

Chlorine nitrate was synthesized by reacting ClF with HNO_3 at 195 K in a stainless steel reactor according to the procedure described by Schack.[36] ClF was prepared as needed by discharging a mixture of Cl_2 and F_2 in He and separating the

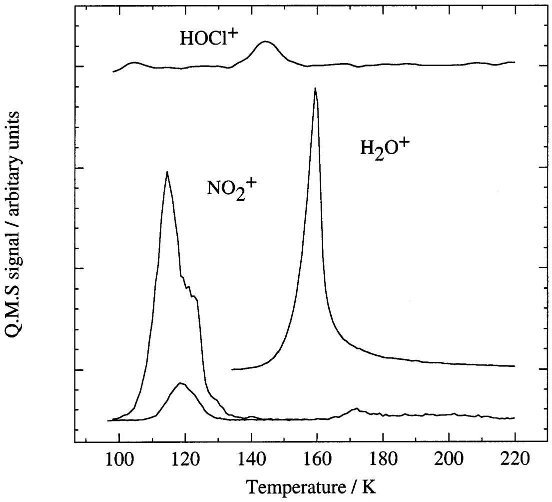

Figure 1. Temperature-programmed desorption spectra of ice dosed with ca. 1.5 ML of $ClONO_2$ at 85 K, taken with a heating rate of 1.4 K s^{-1}. The spectra have not been corrected for the sensitivity of different mass peaks and are offset in the vertical direction for clarity. The mass 46 peaks near 120 K are due to $ClONO_2$, while the small peak at 172 K is due to the desorption of nitric acid. The smaller NO_2^+ peak near 120 K shows $ClONO_2$ desorption from a submonolayer exposure on the ice surface.

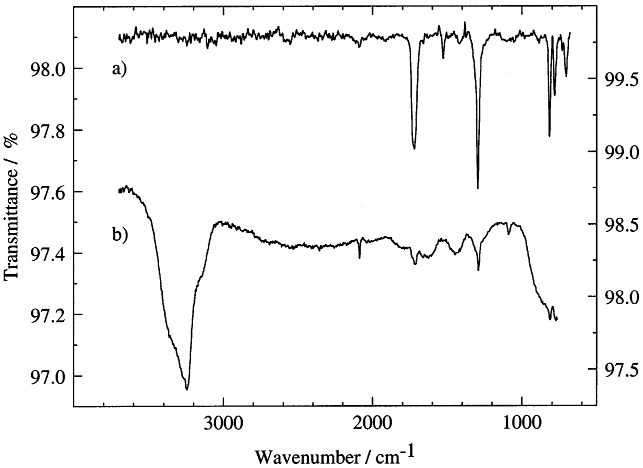

Figure 2. Reflection−absorption IR spectra of (a) a multilayer of $ClONO_2$ adsorbed onto Pt(111) at 90 K, (b) an ice film after exposure to a submonolayer dose of $ClONO_2$ at 90 K.

ClF product by vacuum distillation. The purity of the $ClONO_2$ formed was checked by recording its cracking pattern in a mass spectrometer and the RAIRS spectra of multilayer $ClONO_2$ films grown on the Pt(111) substrate. These were in excellent agreement with those found in the literature with only a very small Cl_2 impurity detected.

3. Results and Discussion

$ClONO_2$ and HOCl both crack to produce the ClO^+ fragment (mass 51) in the mass spectrometer, so the uptake of $ClONO_2$ was monitored using the $^{14}N^{16}O_2^+$ (mass 46) fragment, which is also formed by fragmentation of HNO_3, while the parent ion $^1H^{16}O^{35}Cl$ (mass 52) was used to follow HOCl desorption. During the uptake of $ClONO_2$ onto ($HCl{:}3H_2O$) ice films, chlorine was monitored using the mass 70 parent ion.

(a) Adsorption on Ice I_h Films. Adsorption of $ClONO_2$ at 85 K occurred with an initial sticking probability of 0.98 onto the clean ice surface. $ClONO_2$ uptake continued indefinitely, forming a multilayer on top of the ice film, with no reaction products being desorbed into the gas phase. The temperature-programmed desorption spectrum of $ClONO_2$ adsorbed on ice is shown in Figure 1. This shows the formation of a peak at 120 K due to desorption of molecular $ClONO_2$ from the ice surface, with a multilayer peak near 114 K forming after continued $ClONO_2$ exposure. The 120 K desorption peak accounts for less than 1 ML of $ClONO_2$ and the increased desorption temperature indicates that hydrogen bonding to the underlying surface stabilizes the first layer of molecular $ClONO_2$. After $ClONO_2$ has desorbed there is a peak due to HOCl desorption at 144 K, just prior to the onset of H_2O desorption near 160 K. The desorption of all the HOCl from the ice surface above 150 K is in good agreement with previous studies[18] and confirms that HOCl will not be present in large quantities on the surface under atmospheric conditions. HOCl desorption indicates that reaction has occurred either during adsorption at 85 K or else during the temperature ramp before $ClONO_2$ desorbs. No RAIRS or TPD evidence was found for molecular $ClONO_2$ adsorbed on the surface above 120 K. Once nearly all the water has desorbed, there is a second small peak in the mass 46 trace near 172 K due to HNO_3 desorption. The position of this peak is sensitive to the amount of water on the surface; the nitric acid is strongly hydrated and desorbs only as the last of the water is lost from the surface.

The RAIRS spectrum of a $ClONO_2$ multilayer showed bands at 1719, 1294, 818, 783, and 708 cm^{-1} (Figure 2), consistent with those reported previously.[12] Dosing onto an ice film at 90 K to produce a submonolayer coverage of $ClONO_2$ resulted in the spectrum shown in Figure 2b. In addition to the water bands near 3300, 1627, and 892 cm^{-1} and the molecular $ClONO_2$ bands, there are additional broad bands at 1770, 1440, and ca. 1270 cm^{-1}. These bands are consistent with the presence of hydrated nitric acid on the surface[37] and indicate that some of the $ClONO_2$ has been hydrated even at 90 K. We did not see any clear evidence for bands due to molecular HOCl, although the lower frequency bands are likely to be obscured by nitrate bands, while the band near 2700 cm^{-1} appears to be weak[11] and may be further broadened by the presence of molecular $ClONO_2$. Oppliger et al.[26] found that HOCl production in the gas phase was slow even at 180 K, suggesting that this resulted from slow decomposition of some precursor species, and it is possible that free HOCl does not form immediately during $ClONO_2$ hydration.

Above 120 K, $ClONO_2$ desorption is sufficiently fast compared to the dosing rate to prevent multilayer formation during adsorption measurements. The adsorption probability at 135 K is shown as a function of $ClONO_2$ uptake in Figure 3. The initial sticking probability is unchanged from that at 85 K, with almost every incident $ClONO_2$ becoming adsorbed, and drops only fractionally to $S_o = 0.96$ at 144 K. As expected,[18,21,22,28] no gas-phase products were observed. In the presence of excess surface water $ClONO_2$ hydrates at the ice surface to form nitric acid hydrate and HOCl, with both products remaining condensed on the ice surface.[11,29] For low uptakes the reaction probability remains nearly constant, independent of the $ClONO_2$ uptake, Figure 3, only starting to drop once the uptake has reached half of its saturation coverage. This behavior is characteristic of precursor-mediated adsorption,[38] where the adsorbate traps efficiently into a weakly bound state, often a physisorption state whose steric constraints are relatively weak, followed by transfer into a deeper (chemisorption) well where the adsorbate is localized with a specific orientation and bonding to the surface. Once trapped into the molecular adsorption well, $ClONO_2$ will either desorb back to the gas phase or, if the lifetime of the precursor is sufficient, diffuse across the surface

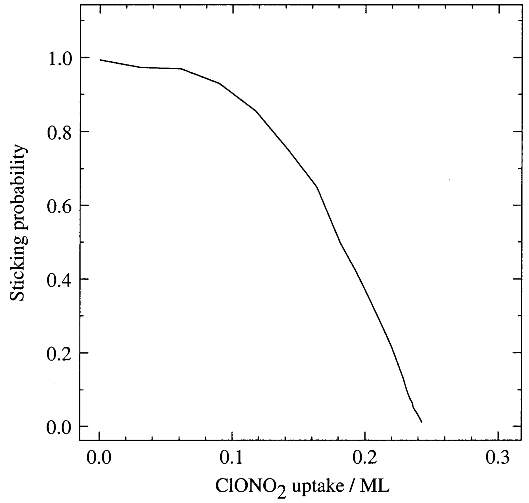

Figure 3. Sticking probability of chlorine nitrate as a function of uptake onto ice at 135 K.

to find a favorable reaction site, so giving rise to the slow decrease in adsorption probability with coverage characteristic of precursor-mediated trapping−dissociation.[38,39]

The molecular $ClONO_2$ TPD peak near 120 K suggests a candidate for this precursor state. However, the surface from which this $ClONO_2$ desorbs is rather different from that of the original ice I_h, since some reaction has already occurred before this species desorbs at 120 K. The molecular $ClONO_2$ which desorbs at 120 K is adsorbed on a surface which is covered with hydration products, probably HOCl and hydrated nitric acid, and so reflects the stability of the extrinsic precursor state[38] (i.e., $ClONO_2$ adsorbed on a region of the surface where reaction has already occurred) rather than the intrinsic trapping state on the clean ice surface. Xu and Zhao[14] suggested that the $ClONO_2$ precursor state was a weakly hydrogen-bonded species, and this is consistent with the increased stability of the surface species compared to the multilayer, Figure 1. A SIMS study by Donsig et al.[40] also found a similar multilayer desorption temperature and suggested a change in the Cl−O bond polarity as the water coordination increased, consistent with the idea of a hydrogen-bonded molecular state. This study did not observe reaction to produce HOCl at low temperature, probably because of the low saturation yield of product.

Although no molecular HOCl desorbs into the gas phase during adsorption below 140 K, HOCl was observed in the TPD spectra of the resulting ice film after saturation with $ClONO_2$ (Figure 4). The uptake of $ClONO_2$ and yield of HOCl were similar whether from multilayer adsorption at low temperature or from dosing at 120 K or above. The saturation uptake of $ClONO_2$ was just (0.25 ± 0.05) ML, any further uptake only occurring slowly with a sticking probability $S < 5 \times 10^{-2}$. The saturation uptake did not change when we increased the thickness of the ice film up to 13 bilayers, consistent with $ClONO_2$ uptake being limited to the surface of the ice film. In fact the saturation uptake of $ClONO_2$ did not increase significantly even when water desorption starts above 144 K, indicating that the reaction products remained on the surface inhibiting further adsorption of $ClONO_2$. At least at these temperatures, chlorine nitrate does not seem to be capable of reacting with water from beneath the top bilayer. This contrasts with the behavior during HCl adsorption, where transport into the bulk is sufficiently fast above 125 K that free water is available at the surface to continue adsorption.[34] George and co-workers have shown that, whereas HCl adsorption increases water diffusion and desorption, nitric acid inhibits both processes,[41,42] nitric acid hydrates forming an immobile, passive film, preventing water from reaching the surface and stopping further reaction.

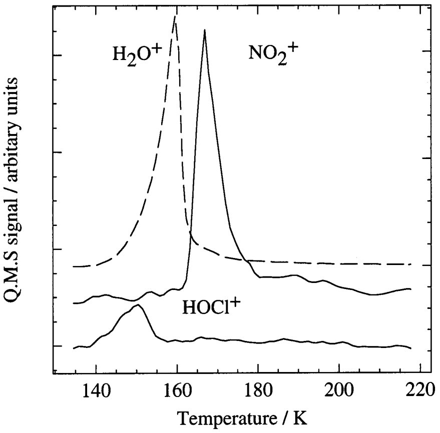

Figure 4. Temperature-programmed desorption spectra for ice exposed to $ClONO_2$ at 135 K. The NO_2^+ peak near 167 K is due to HNO_3 desorption as the last of the water desorbs.

Adsorption on ice films at higher temperatures indicates that reaction forms an acid film with a composition close to $3H_2O$:HNO_3, possibly as NAT or as a supercooled liquid solution with a slightly lower composition.[22,26,43] The thickness of this hydrate film is not known. The rapid poisoning of $ClONO_2$ adsorption at temperatures below 145 K with a surface water-to-nitric acid ratio of 4:1 indicates a hydration stoichiometry which is slightly more dilute, but in this case no HOCl is desorbed from the surface until it is heated above 145 K. We saw no clear evidence for the formation of either molecular HNO_3, which has been seen at high exposures,[11] or crystallization of nitric acid trihydrate on the ice surface.[22] $ClONO_2$ uptake remains the same even for adsorption at 120 K, where the ice surface is essentially immobile, suggesting that the hydrolysis reaction involves only surface water molecules and that incorporation of $ClONO_2$ into the ice film does not play a central role in the reaction. This indicates that $ClONO_2$ can hydrolyze in the presence of just 4 or fewer water molecules and does not require an extended hydrolysis shell for reaction to occur.[16,25]

The large reaction probability found here for (eq 1) at $120 < T < 150$ K is broadly consistent with the high reaction cross section $\gamma_1 > 0.1$ found in flow tube and pulsed dosing experiments at higher temperatures.[22,26,28] At higher temperatures, desorption from the precursor state will start to compete with reaction, producing a characteristic decrease in the reaction probability as the surface temperature is increased. Since we do not observe any change in the adsorption probability below 145 K, we are unable to estimate how much, if at all, the reaction probability drops at higher temperatures.

The sensitivity of $ClONO_2$ reaction to surface nitric acid coverages above 0.1 ML (Figure 3) places a stringent requirement on the cleanliness of the ice surface used in adsorption measurements. An obvious source of surface nitric acid impurity is the presence of a significant level of $ClONO_2$ in the chamber during dosing of H_2O onto the metal substrate. This was clearly the case in previous studies,[18,29] as the authors recognized, but is minimized here by using molecular beam dosing. We believe this may explain the difference between our results for the reaction probability and the much lower values found in a previous LITD study[29] where the authors estimate a nitric acid impurity level of 1 monolayer (or 4%) in their ice films. The values for the reaction probability found there are closer to the values quoted in the literature for reaction of $ClONO_2$ on

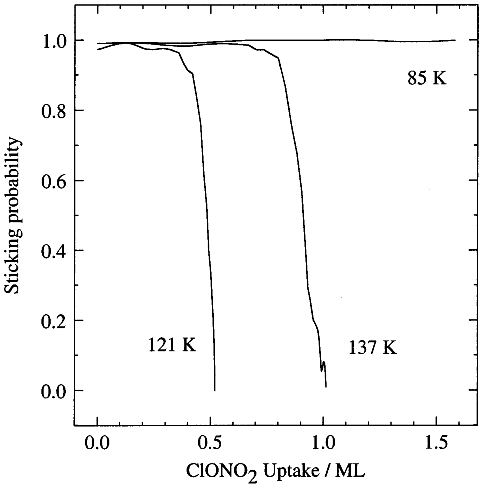

Figure 5. Sticking probability of chlorine nitrate on ($HCl{:}3H_2O$) as a function of $ClONO_2$ uptake and temperature.

NAT,[22,43] and suggest a significant surface nitric acid contamination. Similarly we could see no evidence for the decrease in reaction probability above 120 K reported earlier[29] which prompted suggestions of a change in reaction mechanism to account for the high yield at 180 K. Horn et al.[11] have found that molecular HNO_3 is formed slowly at higher exposures where no free surface water is available for reaction but any slow reaction that continues above 0.25 ML uptake is below our detection sensitivity.

(b) Reaction on $HCl{:}3H_2O$ Films. The sticking probability for $ClONO_2$ on pure ($HCl{:}3H_2O$) ice films is similar to that for reaction on pure ice, $S = (0.98 \pm 0.02)$, Figure 5. At 85 K $ClONO_2$ uptake continues indefinitely forming multilayers, while at temperatures above 120 K $ClONO_2$ sticking remains constant until reaction is nearly complete, before falling abruptly to below our detection limit, $S < 0.05$. Again, this sticking behavior is characteristic of a precursor-mediated mechanism for $ClONO_2$ reaction on ($HCl{:}3H_2O$) ice films, with an initial trapping probability similar to that found on pure ice films. The observation of a similar trapping probability and uptake dependence during adsorption on pure and HCl-saturated ice films is further evidence that $ClONO_2$ traps into a molecular state prior to reacting, as proposed previously.[18,26,27] Unlike adsorption on pure water ice, the saturation uptake of $ClONO_2$ on the ($HCl{:}3H_2O$) films increased with temperature. At 121 K 0.5 ML of $ClONO_2$ was adsorbed before the sticking probability fell too low to measure ($S < 0.05$), while the uptake increased to ~1 ML at 135 K.

As shown in earlier studies of $ClONO_2$ uptake on HCl-doped ice films,[18,26] no HOCl is desorbed during reaction, although at the temperature of these experiments ($T \leq 145$ K) any HOCl produced could remain adsorbed on the surface. The production of Cl_2 is shown in Figure 6 as a function of time during $ClONO_2$ exposure, corresponding to the adsorption behavior shown in Figure 5. Immediate production of Cl_2 is seen at all temperatures, indicating that reaction occurs even at 85 K. TPD analysis of the ice films formed by reaction with $ClONO_2$ shows that whereas all the Cl_2 desorbs directly during reaction at 135 K or above, Figure 7, a significant amount of additional chlorine Cl_2 desorbs as the film is heated following reaction at 120 K or below. A substantial Cl_2 TPD peak is seen near 145 K, with additional desorption occurring between 100 and 120 K following reaction at 85 K. Although $ClONO_2$ uptake at 85 K continues indefinitely to form multilayers, production of Cl_2 in the gas phase drops off at around the same coverage as at 121 K. Combining the Cl_2 yield produced during reaction and evolved in the subsequent TPD, we find that the overall Cl_2 production is consistent with roughly the same amount of $ClONO_2$ having reacted during exposure at 85 K and subsequent multilayer desorption as for reaction at 121 K. Although in all cases a Cl_2 desorption signal appears as soon as $ClONO_2$ exposure starts, the Cl_2 yield does not mimic the $ClONO_2$ sticking behavior exactly. The Cl_2 yield starts to drop well before the $ClONO_2$ sticking probability decreases, and some Cl_2 production continues after $ClONO_2$ adsorption has ceased (Figure 6b). Since molecular Cl_2 desorbs at lower temperature, this delayed signal appears to be due to slow reaction on the surface at $T \leq 120$ K. Desorption of Cl_2 from the reaction of HCl with HOCl/ice films has also been seen when the films were heated between 150 and 170 K.[18]

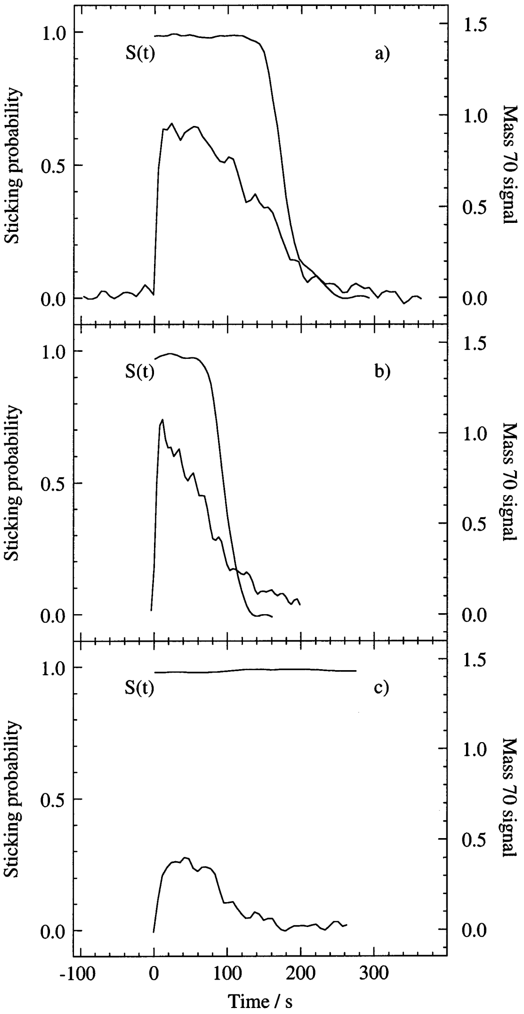

Figure 6. Production of gas-phase Cl_2 from ($HCl{:}3H_2O$) films as a function of the $ClONO_2$ exposure at (a) 137 K, (b) 121 K, and (c) 85 K. The time dependence of the Cl_2 desorption rate (right-hand scale) is shown as a function of the $ClONO_2$ sticking behavior (left-hand scale) after the beam is allowed to hit the surface at $t = 0$.

The immediate formation of gas-phase Cl_2, even at 85 K, is consistent with the current view[18,26,40] that reaction occurs via direct nucleophilic attack of Cl^- on $ClONO_2$. This is supported by recent theoretical work[17,27] which suggests that the reaction takes place directly between Cl^- and a partially ionized precursor $Cl^{\partial+}ONO_2^{\partial-}$ formed by hydration on the surface. The evolution of Cl_2 during annealing of films exposed to $ClONO_2$ at low temperatures is consistent with Cl^- reacting with the $ClONO_2$ hydration products remaining on the surface, either HOCl formed by reaction 1 or direct attack on adsorbed

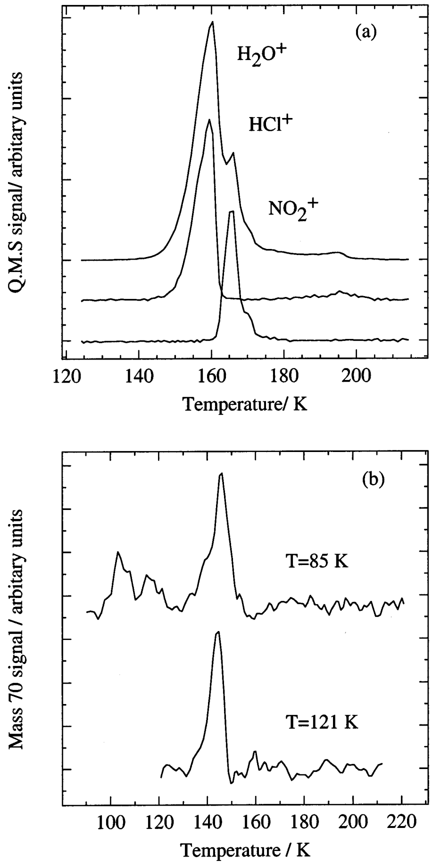

Figure 7. (a) TPD spectra of an ($HCl{:}3H_2O$) film dosed with $ClONO_2$ at 135 K, taken with a heating rate of 1.4 K s^{-1}, showing the desorption of water, HCl, and nitric acid. No HOCl or Cl_2 desorption was observed. (b) TPD spectra of Cl_2 desorption after $ClONO_2$ exposure at 85 and 121 K. The spectra have been offset in the vertical direction for clarity.

$ClONO_2$. The increase in saturation $ClONO_2$ uptake above 121 K appears to be associated with the increased mobility of HCl in ice films above this temperature. Experiments on HCl adsorption and subsequent incorporation into crystalline ice films have shown that adsorption is limited to the ice surface at temperatures below 120 K.[34] At higher temperatures HCl is incorporated rapidly into the bulk, hydration driving HCl transport through 100's of bilayers by 137 K. However, unlike HCl hydration, the $ClONO_2 + HCl$ reaction 3 remains confined to the near surface layers, with reaction being inhibited after ~1 ML of $ClONO_2$ has adsorbed. This corresponds to reaction with the Cl^- content of several layers of ice[33] before the buildup of nitric acid hydrates effectively poisons further reaction. In contrast, reaction 1 between $ClONO_2$ and H_2O involves only the surface water molecules.

4. Conclusion

We have shown that the uptake of $ClONO_2$ on ice and ($HCl{:}3H_2O$) films between 85 and 145 K occurs by a precursor mechanism, with a reaction probability which is close to unity on both surfaces. On crystalline ice the reaction probability for $ClONO_2$ was 0.96 at temperatures below 144 K, adsorption saturating at a coverage of 0.25 ML. This uptake did not change with temperature and is consistent with reaction involving only the surface water bilayer, to form a surface film with a composition of $HNO_3{:}HOCl{:}4H_2O$. This stoichiometry suggests formation of an amorphous nitric acid trihydrate, consistent with the composition found at higher temperature,[21,22] with HOCl probably hydrogen bonded to the additional surface water molecule.[19,20] The reaction probability for $ClONO_2$ on ($HCl{:}3H_2O$) was 0.98 for all temperatures between 85 and 137 K, with no indication of any decrease at higher temperatures. The uptake of $ClONO_2$ on ($HCl{:}3H_2O$) films increased with temperature above ca. 120 K, the temperature at which HCl starts to become mobile in ice films. However, $ClONO_2$ reaction remains confined to the near surface region (top 3 layers or so) and there is no significant transport into the ice film. The reaction of $ClONO_2$ on ($HCl{:}3H_2O$) produces gas-phase Cl_2 immediately after exposure, consistent with existing models of a direct reaction between the $ClONO_2$ precursor and Cl^- present on the ice surface, but below 120 K the reaction becomes slow and an increasingly large fraction of the Cl_2 is produced only when the film is annealed, allowing buried Cl^- to react.

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