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Heterogeneous Reactions of Chlorine Peroxide with Halide Ions

D. O. De Haan* and J. W. Birks

Cooperative Institute for Research in Environmental Sciences (CIRES) and Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0216

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The heterogeneous reactivity of chlorine peroxide (ClOOCl) on halide-doped ice surfaces was studied using discharge-flow mass spectrometry over the temperature range 209−258 K. By monitoring $Cl_2O_2^+$ parent ion signals, reactions were observed on ice doped with I^-, Br^-, Cl^-, or F^- ions. XCl was the only gas-phase product detected in each reaction, where X = dopant halide. Other products evidently remain bound at the ice surface and were not detected. The heterogeneous reaction $ClOOCl + X^- \rightarrow XCl +$ products is proposed. Chloride-doped ice layers were made either by freezing aqueous solutions of HCl or NaCl on the flow tube walls or by adding HCl gas to pure ice layers. Thermodynamic considerations indicate that reaction surfaces below the NaX/H_2O systems' eutectic points were mixtures of two solid phases (ice and NaX hydrate crystals), while liquid layers existed at HCl/ice surfaces under our conditions. Our measured ClOOCl reaction probabilities on solid surfaces ranged from $\gamma = 0.026$ to $\gamma \geq 0.3$ on NaI/ice surfaces, from $\gamma = 0.0016$ to $\gamma = 0.064$ on NaBr/ice surfaces (possibly temperature dependent), from $\gamma = 0.0009$ to $\gamma = 0.0092$ on NaCl/ice surfaces, and from $\gamma = 0.0006$ to $\gamma = 0.0050$ on NaF/ice surfaces. ClOOCl reaction probabilities measured on HCl/H_2O liquid layers were as high as $\gamma = 0.0065$, and on pure ice surfaces as high as $\gamma = 0.0011$. In the absence of halide ions, there was no detectable reaction of ClOOCl on ice doped with nitric or sulfuric acid ($\gamma \leq 4 \times 10^{-4}$). Chlorine peroxide uptake was heavily time-dependent, especially on HCl/ice surfaces, indicating that these measurements of heterogeneous kinetics were limited by saturation and deactivation effects in the flow tube. Stratospheric reaction probabilities may therefore differ from those reported here.

1. Introduction

The chemical mechanisms causing polar stratospheric ozone depletion have been intensively studied for several years.[1] It is generally agreed that enhanced levels of chlorine in the atmosphere caused by the release of chlorofluorocarbons are responsible for most of the ozone destruction in this region.[2] Heterogeneous (surface) chemistry activates chlorine from its reservoir species ($ClONO_2$ and HCl) and sequesters oxides of nitrogen as HNO_3 on particle surfaces, making it possible for chlorine to catalyze rapid ozone destruction after sunrise[3] mainly by the following mechanism:[4]

$$ClO + ClO + M \leftrightarrow ClOOCl + M \qquad (1)$$

$$ClOOCl + h\nu \rightarrow Cl + ClOO \qquad (2)$$

$$ClOO + M \rightarrow O_2 + Cl + M \qquad (3)$$

$$2(Cl + O_3 \rightarrow ClO + O_2) \qquad (4)$$

$$\text{Net:} \quad 2O_3 \rightarrow 3O_2$$

In this paper we present the first experimental evidence for heterogeneous reaction pathways of chlorine peroxide (ClOOCl), a key intermediate in the above cycle:

$$ClOOCl_{(g)} + X^-{}_{(c)} \xrightarrow{\text{ice}} XCl_{(g)} + \text{products}_{(c)} \qquad (5)$$

where X = any halogen atom, the subscript (g) refers to a gas-phase species, and the subscript (c) identifies condensed-phase species. Thus, $X^-{}_{(c)}$ represents a halide ion either at a solid surface or in a surface liquid layer. We will use (s) and (l) to refer specifically to solid or liquid phase species. Evidence is presented that chlorine peroxide will react with iodide, bromide, chloride, or fluoride ions at ice surfaces, activating these halides to the photolytically active mixed halogen gases XCl. We are unable to identify any condensed-phase products, since reactive surfaces could not be directly observed in the experiments reported here.

Trajectory modeling studies have shown that reaction 5 (with X = Cl) may affect the partitioning of chlorine species, and therefore ozone depletion rates, in the Arctic stratosphere if two conditions are met: first, the reaction probability, γ, of ClOOCl on PSC (polar stratospheric cloud) surfaces must be greater than 0.03, and second, all three halide atoms involved in the reaction must be activated at the end of the reaction sequence.[5] The idea of a heterogeneous reaction of the form

$$ClOOCl + HCl \rightarrow Cl_2 + HOOCl \qquad (6)$$

was suggested in 1988 by Wofsy et al.[6] as an acid-catalyzed ice surface reaction. The proposed pathway for chlorine activation[5] involves the formation and subsequent photolysis of HOOCl:

$$HOOCl + h\nu \rightarrow Cl + HO_2 \qquad (7)$$

Ab initio calculations indicate that HOOCl is a stable gas-phase compound, which might be expected to photolyze by analogy with either HOOH or ClOOCl.[7] However, since the molecule HOOCl has not yet been observed, the existence of this pathway remains uncertain.

Past studies of the heterogeneous kinetics of $ClONO_2$ and N_2O_5 have found that these compounds are reactive toward both HCl (at ice surfaces)[8−11] and NaCl,[12,13] and toward both HBr[14] and NaBr.[15] Chlorine nitrate is even reactive toward gas-phase chloride ions.[16] In the reactions with the acids, a mechanism

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* Corresponding author. Current address: Department of Chemistry and Biology, Lyon College, 2300 Highland Rd., Batesville, AR 72503.

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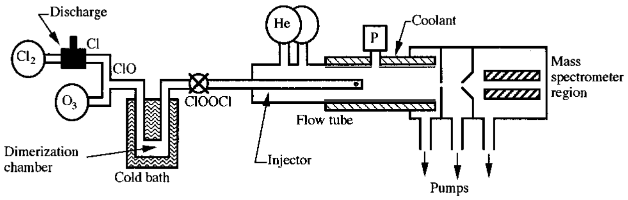

Figure 1. Schematic diagram of discharge-flow/mass spectrometry apparatus for measuring the heterogeneous reaction rates of chlorine peroxide. Glassware designed for the flowing synthesis of ClOOCl is shown on the left side of the diagram; synthesis conditions are described in section 2.2. In certain experiments the ozone bulb was replaced by a chamber holding powdered HgO. A slow flow of chlorine passed through the chamber forms ClOCl, which also reacts with chlorine atoms to form ClO radicals.

where the reactive species at the surface are dissociated halide ions has been proposed.[17] Recent studies of the uptake of NO_2, HNO_3, and N_2O_5 on NaCl surfaces have shown that small amounts of strongly adsorbed water at the surface control the reactivity of the surfaces.[13,18−20] These small aqueous regions, which tend to exist at crystal edges and defect sites on the salt surface, are saturated with halide ions. Since in all these cases it appears that halide ions are the reactive species, ice surfaces have been doped with either acids or salts containing halide ions in this study. Kinetic data describing ClOOCl uptake onto halide-doped ice surfaces are presented, but application of the data is limited by evidence of saturation or deactivation of the reactive surfaces.

2. Experimental Section

2.1. Apparatus. All experiments were performed using a discharge-flow system modified from one described earlier.[21] The cylindrical flow tube was coupled to a differentially pumped quadrupole mass spectrometer (UTI Model 100C), Figure 1. A movable injector tube allowed reaction times to be varied. The last 70 cm of the flow tube was cooled to as cold as 209 K by circulating nitrogen gas through a Pyrex spiral flow cooling jacket. Three copper-constantan thermocouple junctions monitored temperatures, which varied by less than ±2 °C along the length of the tube. (All errors are given as $\pm 2\sigma$ unless otherwise noted.) Flow tube pressures were monitored to ±0.001 Torr by a capacitance manometer (MKS Baratron). Helium flow rates were measured by a 2 L/min (Tylan FC-260) mass flow controller; flow tube pressures ranged from 2.2 to 6.9 Torr. Pressures in the diffusion-pumped mass spectrometer were between 10^{-5} and 10^{-6} Torr during experiments, depending on helium flows and pumping speeds.

2.2. Preparation of Reaction Surfaces and Reagents. Reaction surfaces doped with halide ions were made by brushing aqueous sodium halide solutions (0.1−2.0 M NaX) or HCl solutions (≈2 M) onto precooled (≈230 K) flow tube walls. Mixtures of H_2SO_4/H_2O or HNO_3/H_2O were also introduced into the flow tube in this manner. The bulk freezing process was fast enough that solutions generally froze in place in the horizontally oriented flow tube, but surfaces were occasionally observed to be thicker along the bottom of the tube. In other experiments, HCl/H_2O and HF/H_2O surfaces were created by flowing gas-phase HX/He mixtures (both before and during measurements) over a layer of H_2O ice already in place. The partial pressures of hydrogen chloride gas, when added, ranged from 0.004 to 0.06 Torr. According to the HCl/H_2O phase diagram published by Wooldridge et al.,[22] these gas-phase HCl additions would have melted the ice surfaces and formed liquid HCl/H_2O layers.

To understand the nature of the NaX/ice reaction surfaces, we must consider the freezing process of solutions. The amount of HCl incorporated into ice forming out of HCl/H_2O solutions is small, with an HCl concentration in the bulk ice that is only 25% of that in the initial solution.[6] Similarly, when a solution of NaX and water is frozen at 1 atm, the exclusion of ions from the ice will concentrate Na^+ and X^- ions into a shrinking solution layer. The concentration of NaX in this layer will increase as the temperature drops until the eutectic point is reached. At this point, three phases coexist (see Table 1): a liquid phase of known concentration, ice, and hydrated salt crystals.[23,24] As more heat is removed from the system, the temperature remains constant at the eutectic point until all of the salt solution is converted into the two solid phases, ice and salt hydrate. Only then can the temperature drop below this value. Supercooling in the NaI/H_2O system has been observed only when the starting NaI concentration in solution is greater than the eutectic concentration,[23] a situation that does not apply to the NaX/H_2O surfaces described here. To our knowledge the eutectic behavior of NaX/H_2O systems has not been measured below ambient pressures; however, since the melting point of ice increases by only 0.01 °C between 760 and 5 Torr,[25] we do not expect the eutectic temperatures and concentrations at low pressures to change significantly from those given in Table 1.

TABLE 1: Temperatures, Liquid-Phase Compositions, and Salt Hydrate Formed for Three NaX/H_2O Systems at the Eutectic Point at 1 atm[23−25]

system	eutectic point temperature (K)	liquid-phase composition at eutectic point (wt % salt)	salt hydrate formed at eutectic point
$NaCl/H_2O$	252.0	23.3	$NaCl{\cdot}2H_2O$
$NaBr/H_2O$	245.1	40.3	$NaBr{\cdot}5H_2O$
NaI/H_2O	241.6	39.0	$NaI{\cdot}5H_2O$

Since the ice freezing process is nucleated at the flow tube wall, during the cooling process NaX solution is expected to exist in a layer at the surface of the ice and embedded in concentrated pockets inside the ice. For temperatures at or above the eutectic point of the system, the reaction surface is therefore expected to be a liquid layer of concentrated NaX solution, where the NaX concentration is given by the liquidus line separating the solution and ice/solution coexistence areas of the phase diagram of the system.[24] Below the eutectic temperature the reaction surface must be made up of a mixture of salt hydrate crystals and ice. Because of significant amounts of water vapor in the flow tube, the salt hydrate crystals may, in turn, contain strongly adsorbed water on their surfaces which may alter the level of surface reactivity.[19,26] The rate of cooling during the ice freezing process may influence the amount of salt that is embedded in the bulk ice and, correspondingly, the surface coverage of the salt crystals on the ice surface. Since the cooling rate was not controlled in these experiments, variations in salt crystal coverage at the surface appear to have been a dominant form of chemical noise in the gas uptake measurements.

Ice layer thickness varied from 300 to 900 μm and had no discernible effect on ClOOCl reaction rates. Geometric flow tube surface areas were therefore used to compute ClOOCl uptake. Starting experiments with thick ice layers was necessary because of constant water sublimation into the gas phase, which was not presaturated with water vapor.

Dry coatings of NaCl and NaBr were formed from NaCl/ice and NaBr/ice layers by turning off the flow tube cooling system and pumping away the subliming water vapor. Resulting layers of salt residue in the flow tube were visually well-distributed. Since the salt residues were not baked, the salt surfaces may have contained submonolayer amounts of strongly adsorbed water, especially at salt crystal defect sites.[19]

Chlorine peroxide was synthesized in a discharge-flow system designed to emulate the conditions of Cheng and Lee.[27] A schematic diagram of the system is included in Figure 1. The reaction sequence for ClOOCl production was as follows:

$$Cl_2 \xrightarrow{\text{microwave discharge}} 2Cl \tag{8}$$

$$Cl + O_3 \rightarrow ClO + O_2 \tag{4}$$

$$ClO + ClO + M \leftrightarrow ClOOCl + M \tag{1}$$

Excess ozone must be present in the flow tube to scavenge chlorine atoms, which can catalyze gas-phase decomposition of chlorine peroxide.[28] In certain experiments, chlorine peroxide was also synthesized using dichlorine monoxide (ClOCl) instead of ozone as a precursor. However, excess ClOCl reacted at halide-doped ice surfaces at approximately the same rates as ClOOCl itself and was shown to greatly interfere with kinetics measurements of ClOOCl uptake.

Chlorine gas (Matheson, high purity) was diluted in helium (US Welding, 99.999%) and stored in stainless steel bulbs (approximately 35 L), at concentrations between 3.1 and 6.4% Cl_2 and at total pressures up to 50 psi. Ozone was made using a discharge-type ozone generator (Pillar Technologies) and UHP oxygen, trapped at 196 K on silica beads, then diluted and stored in a passivated, black-taped glass bulb at concentrations between 0.4 and 0.9% O_3 in He, with total pressures below 20 psi. Ozone bulbs were used for no more than 3 days after being filled, because of ozone loss by wall reactions. Flow rates through the microwave discharge region were as follows: total helium, 100−500 standard cm^3/min (sccm); chlorine gas, 0.2 sccm.

The microwave discharge formed chlorine atoms at an efficiency ranging from 1 to 20%, averaging about 4%, depending on the freshness of the phosphoric acid coating on the wall of the discharge tube and on the pressure. All glass surfaces between the microwave discharge region and the flow tube itself were coated with halocarbon wax (Halocarbon Products Corp.) to slow ClOOCl surface decomposition.[28]

The formation of chlorine peroxide is a slow dimerization with several bimolecular channels in competition.[29,30] Cold temperatures and high total pressures heavily favor ClOOCl formation. An in-line U-shaped tube with a restricting valve at the outlet (to vary the pressure and residence times), cooled to between 200 and 230 K in a Dewar flask, served as the dimerization chamber in these experiments. Optimal pressures in the dimerization chamber were between 8 and 20 Torr; at 210 K, this pressure range allows the dimerization to proceed at a rate 10−24 times that of all three bimolecular channels combined.

During a typical residence time of about 0.5 s, calculations by the GEAR chemical simulation program indicate that 60% of ClO radicals react to form chlorine peroxide, while only negligible amounts of bimolecular reaction products are formed. Chlorine peroxide concentrations in the flow tube were calculated to be in the range $10^{11}-10^{13}$ molecules cm^{-3} using recommended rate coefficients.[31] The GEAR program was also used to establish upper limits on errors in the measured ClOOCl loss rate of ≤7% (negative) caused by formation of ClOOCl from dimerization of ClO within the flow tube and ≤4% (positive) caused by catalytic gas-phase loss due to chlorine atoms at our conditions.

2.3. Kinetics Measurements. ClOOCl was introduced via the injector into the well-characterized bulk helium flow of the flow tube. The "plug flow" approximation was used to compute linear velocity.[32] Calculated velocities were between 1.4 and 7.7 m/s, with total gas flow rates between 0.3 and 1.8 standard liters per minute (slm), the bulk of which was helium flow.

Chlorine peroxide was detected in the quadrupole mass spectrometer by selectively monitoring its parent ion peak, $Cl_2O_2^+$, at $m/z = 102$ using an electron impact energy of 41−44 eV. With peak resolution reduced slightly by varying the rf/dc voltage ratio, signal-to-noise ratios of greater than 100—enough to measure first-order $Cl_2O_2^+$ decay rates accurately—were routinely achieved.

Larger Cl_xO_y species, if formed in amounts comparable to ClOOCl, can potentially interfere with kinetics measurements by generating extraneous $Cl_2O_2^+$ fragments through cracking in the ion source of the mass spectrometer. However, the formation of such compounds depends on the formation of OClO from the bimolecular ClO + ClO channels;[27] thus, because of the selectivity of the conditions used, no more than 5% of the $Cl_2O_2^+$ signal is likely to be due to a fragment from a larger compound. As expected, no Cl_xO_y signal peaks were detected beyond $m/z = 106$ ($^{37}Cl_2O_2^+$).

Ice sublimation can contribute significant uncertainty to linear velocity calculations.[33] In these experiments, since the total gas flow rate was monitored indirectly by pressure (after a daily calibration), the water vapor desorbed from the ice by the time a "gas plug" reached the pressure transducer (≈10 cm from the end of the flow tube) was automatically included into the flow rate calculation, thus minimizing uncertainties. Measurements of the changes in flow tube pressure as temperature was varied indicated that flow tube gases typically held an amount of water vapor 3−4 times below the saturation limit. In other words, water vapor desorption from the ice exceeded water adsorption over the entire flow tube surface.

Surface saturation and deactivation processes caused time-dependent ClOOCl uptake in most runs; to minimize this effect, the changes in ClOOCl signals immediately before and after the injector movement (S_0 and S_1), rather than steady-state signal levels, were used to calculate rate coefficients. The relative signal drops ($\ln S_0 - \ln S_1$) were graphed versus the change in time represented by each injector movement in a series. The slope of the linear least-squares fit (without intercept) to this data set is the measured rate coefficient k_m. Because of variability in surface conditions and saturation rates along the length of the flow tube, the average uncertainty in k_m extracted from a single set of measurements was estimated as $\sigma = \pm 23\%$.

Desorption of chlorine peroxide from the reactive surface was not observed as the injector was pushed back in after each uptake measurement. This suggests that chlorine peroxide uptake onto (both solid and liquid) halide-doped ice surfaces was irreversible, and so we express the rate coefficient as a surface reaction probability. This term is independent of reactor geometry:[34]

$$\gamma = \frac{2k_m r}{\bar{\omega}} \tag{9}$$

where r is the flow tube radius (1.20 cm), $\bar{\omega}$ is the average molecular velocity of ClOOCl, and the reactive ice surface area is assumed to be the geometric surface area of the flow tube. Under most conditions, γ values must be corrected for departures from the plug flow model. The combined effects of parabolic flow profiles, axial and radial concentration gradients, and diffusion of the reactant being measured must be considered. ClOOCl diffusion coefficients were estimated in He and in H_2O vapor.[35] These coefficients were used to calculate ternary diffusion coefficients for ClOOCl in helium/water vapor mixtures,[33] which were between 40 and 80 cm^2/s for most runs. The presence of water vapor lowered the diffusion coefficient by an average of 5.6%. This effect was temperature-dependent,

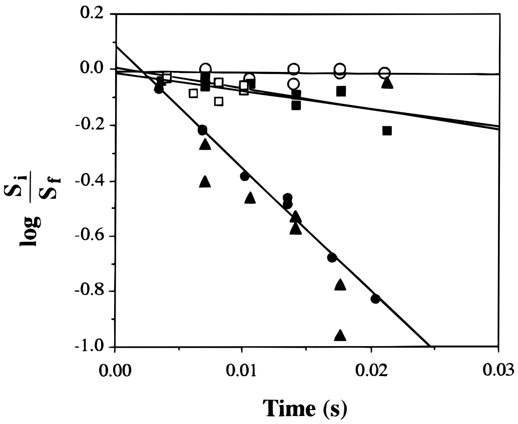

Figure 2. Sample ClOOCl signal losses observed on chloride-doped and halide-free surfaces. Values on the time axis represent changes in reaction time caused by each movement of the flow tube injector. Changes in signal are determined by signal strengths immediately before (S_i) and after (S_f) injector movements, to capture transient changes in the signal and limit the influence of surface deactivation. Open circles: Uncoated Pyrex surface (229 K, $\gamma \leq 4 \times 10^{-4}$). Filled squares: Ice surface (226 K, $\gamma = 8 \times 10^{-4}$). Open squares: Dry NaCl residue (253 K, $\gamma = 8 \times 10^{-4}$). Filled circles: NaCl·2H$_2$O/ice surface (241 K, $\gamma = 5 \times 10^{-3}$). Filled triangles: HCl/ice surface (233 K, $\gamma = 4 \times 10^{-3}$).

as the amount of water vapor increased with increasing temperatures (in proportion to ice vapor pressures).

No corrections for axial diffusion were made since errors in the rate coefficient[36] were calculated to be ≤8% (positive). Radial diffusion limitations were more significant, and all ClOOCl rate coefficients were corrected for this effect.[37] Correction factors depend heavily on the diffusion coefficient and become very large and uncertain as observed rates approach the radial diffusion limit,[33] which is $\gamma \approx 0.02$ for ClOOCl in this system. Observed rates near this limit were corrected to γ as large as 0.3. A few runs slightly exceeded calculated radial diffusion limits, likely due to uncertainty in the estimated diffusion coefficients and the data extraction procedure, and were assigned a corrected surface reaction probability of $\gamma \geq 0.3$. The reaction probability "detection limit" for chlorine peroxide is $\gamma \approx 3 \times 10^{-4}$, limited by noise in the $Cl_2O_2^+$ signal and maximum injector movements of 6 cm.

3. Results

3.1. Reactions with Ice, NaCl, and HCl. Chlorine peroxide signals were observed to decrease and molecular chlorine was produced, upon contact with ice doped with chloride ions. Typical decays in $Cl_2O_2^+$ signals are shown in Figure 2, expressed as instantaneous changes in signal versus the increases in reaction time represented by each injector movement. Samples of $Cl_2O_2^+$ signal decay data are shown for measurements on the glass flow tube wall, a pure ice surface, dry NaCl salt residue, and ice surfaces that have been doped with HCl or NaCl. There was no observable reaction in an uncoated flow tube, even when gas-phase HCl was added to the system, demonstrating that ClOOCl does not decompose at a measurable rate under our experimental conditions in either a gas-phase reaction or at the glass flow tube wall. There was also no observable reaction on dry NaCl residue; however, the upper limit for ClOOCl uptake on such a surface based on this observation ($\gamma \leq 8 \times 10^{-4}$) was higher than the usual limit due to fast linear flow velocities.

Unlike on glass or dry NaCl surfaces, there was a small observable uptake of ClOOCl on pure ice, with $\gamma_{avg} = (5.1 \pm 3.9) \times 10^{-4}$ ($\pm 1\sigma$). The addition of chloride ions to the reaction system caused a further increase in chlorine peroxide uptake, to $\gamma_{avg} = (3.5 \pm 2.1) \times 10^{-3}$ ($\pm 1\sigma$) for the reaction on NaCl-doped ice surfaces. The data are perhaps most usefully summarized by range: ClOOCl reaction probabilities observed on solid NaCl/ice surfaces in the temperature range 211−248 K varied by an order of magnitude, from $\gamma = (9 \pm 1) \times 10^{-4}$ to $\gamma = (9 \pm 1) \times 10^{-3}$. Even with this variability it can be stated that ClOOCl reaction probabilities on ice doped with NaCl increased relative to those on pure ice surfaces (the data sets are statistically distinguishable) at the 99.5% confidence level. A typical set of measurements from a single experiment made on a single NaCl/ice surface had good consistency, as can be seen from stated uncertainties on the high and low values; nevertheless, the ClOOCl uptake varied from surface to surface.

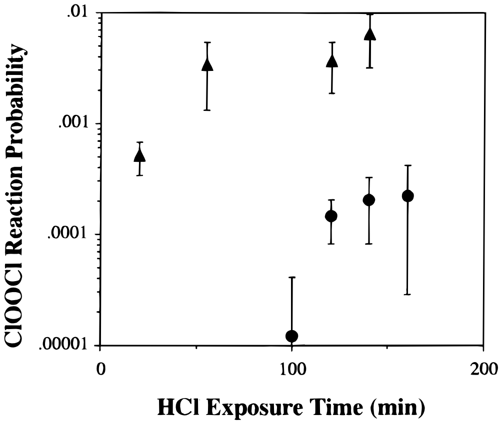

Figure 3. Example changes in chlorine peroxide reaction probabilities on ice as gas-phase HCl/He mixtures are added. An induction period is observed between the introduction of HCl to the bulk flow of the flow tube and the resulting increase in ClOOCl uptake. Error bars reported in this and subsequent graphs are $\pm 2\sigma$ based on the statistical uncertainty in extracting the pseudo-first-order rate coefficient k_m from the data. Triangles: [HCl] = 0.026 Torr. Circles: [HCl] = 0.016 Torr. In this example chlorine peroxide uptake reaches the reaction detection limit only after 2 h of HCl flow.

Doping ice layers with HCl/He gas mixtures (thereby melting the surface) also increased ClOOCl uptake relative to that observed on pure ice surfaces, as seen in the sample data shown in Figure 2. As with the NaCl/ice data, measured ClOOCl uptake rates exhibited great variability, depending on both the HCl concentrations used and on cumulative doping time, as shown in Figure 3. Variations in chlorine peroxide uptake rates were observable along the length of the flow tube (see Figure 2), indicating that the long HCl doping times needed to trigger ClOOCl uptake were due to high losses of HCl onto the ice at the entrance of the flow tube ($\gamma_{HCl} \geq 0.3$) and slow transport down to the reaction zone. Chlorine peroxide reaction probabilities ranged from runs where there was no detectable uptake (typically after short HCl doping times) to runs with surface reaction probabilities as large as $\gamma = 0.0065$. The existence of liquid layers at the ice surface can be expected to affect both the magnitude and the reproducibility of ClOOCl uptake rates. Since the solubility and the diffusion coefficients of chlorine peroxide in concentrated HCl/H$_2$O solutions are not known, it is unclear whether uptake is caused by reaction at the surface or in the bulk of the liquid phase.

No reaction was observed on other types of surfaces which did not contain halide ions, such as a cooled 37% w/w solution of H_2SO_4/H_2O or a cooled 1:3 HNO_3/H_2O solution (possibly NAT). Upper limits for chlorine peroxide uptake probabilities are $\gamma \leq 3 \times 10^{-4}$ for both of these surfaces. In an experiment where gas-phase HCl was added to the sulfuric acid/water mixture at 227 K, ClOOCl was taken up with a reaction probability of 3×10^{-3}.

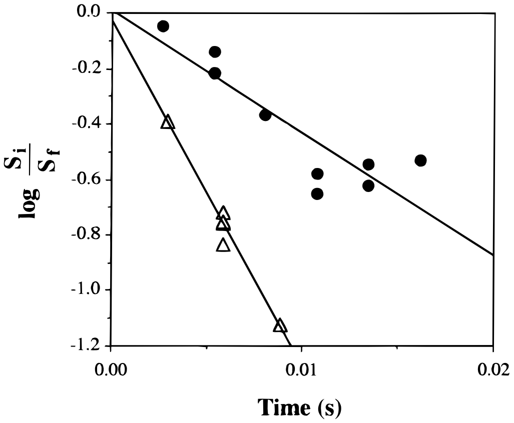

Figure 4. Sample ClOOCl signal losses observed on NaI/ice and NaBr/ice surfaces. Axes are defined as in Figure 2. Circles: $NaBr{\cdot}5H_2O$/ice surface (224 K, $\gamma = 7 \times 10^{-3}$). Triangles: NaI/ice surface (245 K, $\gamma = 1.2 \times 10^{-1}$). The measurement on the NaI/ice surface is above the eutectic temperature of the NaI/H_2O system and so is likely affected by an extensive surface liquid layer of concentrated NaI solution. Note that ClOOCl reaction probabilities on the solid mixture NaBr/ice surface show more variability than on the liquid layer of NaI solution.

Under most conditions the chloride-ion-doped ice surfaces showed clear signs of surface deactivation as they were exposed to chlorine peroxide. Below 246 K, chlorine peroxide uptake rates onto all chloride-doped ice surfaces would decline with time, as would product Cl_2 signals, reaching a lower "steady-state" reaction rate within a minute or less. In all experiments performed on (liquid) HCl/ice surfaces, and on (solid) NaCl/ice surfaces when the flow tube temperature was below 220 K, chlorine peroxide uptake stopped completely after the first exposure of the surface on a time scale of minutes.

Molecular chlorine was verified as a product by mass spectrometry during the reaction of chlorine peroxide with chloride-doped ice surfaces. No other gas-phase products were found. The Cl_2^+ ion signals observed in the mass spectrometer at $m/z = 70$ increased immediately when new reaction surface was exposed, and then also decreased with time as the surface was deactivated, mirroring the declines in ClOOCl uptake. This demonstrates that observed Cl_2 signals were not merely due to ClOOCl fragmentation in the mass spectrometer, nor were they due to only leftover Cl_2 coming through the microwave discharge (a background signal which remained constant as the injector was moved). Instead, it is concluded that molecular chlorine was produced via a surface chemical reaction or decomposition in the flow tube.

Ozone uptake rates onto NaCl/ice surfaces were measured to check the possibility that Cl_2 signals may have been produced by the oxidation of surface chloride ions by ozone. Such a reaction might be analogous to the liquid-phase oxidation of bromide by ozone, which is known to produce HOBr.[38,39] No ozone uptake was observed, which is consistent with observations that ozone reacts with aqueous ClO^- but not Cl^-.[40,41] We set upper limits on ozone uptake probabilities of $\gamma \leq 2 \times 10^{-4}$ at 270 K, decreasing to $\leq 5 \times 10^{-5}$ at 220 K, and conclude that gas-phase Cl_2 is in fact produced by a process involving ClOOCl at the chloride-doped ice surface:

$$\mathrm{ClOOCl} + \mathrm{Cl}^-_{(c)} \xrightarrow{H_2O} \mathrm{Cl}_2 + \mathrm{products}_{(c)} \qquad (5a)$$

TABLE 2: Summary of Ranges of Chlorine Peroxide Reaction Probabilities (γ) Measured on Various Surfaces in This Work

surface	low γ	uncertainty[i]	high γ	uncertainty[i]
HCl/ice[a]	<0.0003[f,g]		0.0065	$f = 1.7$
HF/ice[b]	0.0004[h]	$f = 1.4$	0.0027[h]	$f = 1.6$
NaI/ice[c]	0.026	$f = 1.4$	>0.3	+0.7 −0.22
NaBr/ice[c,d]	0.0016	$f = 1.2$	0.064	$f = 1.5$
NaCl/ice[c]	0.0009	$f = 1.15$	0.0092	$f = 1.11$
NaF/ice[e]	0.0006	$f = 1.5$	0.0050	$f = 1.5$
ice	<0.0003[f]		0.0011	$f = 1.3$
dry NaCl			<0.0008[f]	

[a] Surface liquid layer likely. [b] Surface phase unknown. [c] Solid mixtures, data from below eutectic point only. [d] Possibly temperature-dependent. [e] Solid mixture likely. [f] No detectable reaction. [g] After short HCl exposure times. [h] Measured in the presence of excess ClOCl, which interferes with ClOOCl uptake. [i] ($\pm 2\sigma$). Symmetrical uncertainties are expressed as the factor f where $(\gamma + 2\sigma) = \gamma f$ and $(\gamma - 2\sigma) = \gamma/f$.

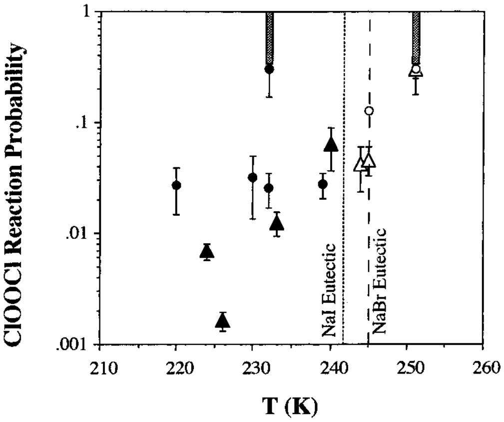

Figure 5. Summary of chlorine peroxide reaction probabilities measured on NaI/ice and NaBr/ice surfaces. Repeated measurements below 225 K were dropped from these data sets, due to long-term surface deactivation. Triangles: NaI/ice surfaces. Circles: NaBr/ice surfaces. Open: Measurements on liquid layers (at or above the eutectic temperature of the system). Filled: Measurements on solid surfaces (below eutectic temperature). The error bars of the top three points (two are overlapping) have been enlarged to indicate $\gamma \geq 0.3$ and the large uncertainties introduced by the radial diffusion correction near the diffusion limit.

3.2. Reactions with NaBr and NaI. Reactive uptake of chlorine peroxide was observed on any surface that contained bromide or iodide ions. Sample data sets for $Cl_2O_2^+$ signal decay on these surfaces are shown in Figure 4. Unlike on dry NaCl surfaces, losses of ClOOCl (in excess ClOCl) were observed on dry NaBr salt surfaces and matched the rates measured on NaBr/ice surfaces in excess ClOCl.[42] Dry salt surfaces were totally deactivated during exposure to ClOOCl, and no uptake was observed upon repeated exposures.

Chlorine peroxide uptake rates were clearly greater on bromide- and iodide-doped ice surfaces than on chloride-doped ice surfaces (see Table 2). Uptake probabilities on solid NaBr/ice surfaces (Figure 5) ranged from $\gamma = (1.6 \pm 0.3) \times 10^{-3}$ at 226 K to $(6.4 \pm 2.7) \times 10^{-2}$ at 240 K. Ice surfaces doped with sodium iodide were the most reactive surfaces studied (Figure 5). The smallest observed chlorine peroxide uptake probability on this type of surface was $\gamma = (2.7 \pm 1.2) \times 10^{-2}$; however, in two runs chlorine peroxide was taken up so rapidly that the rate was diffusion-limited ($\gamma \geq 0.3$). The reaction probabilities measured on solid NaI/ice surfaces are very similar except for the diffusion-limited run at 232 K. This outlying point is probably caused by variability in the NaI/ice surface formation process.

Halogen gases were produced as ClOOCl was taken up on ice doped with bromide or iodide ions. Both bromine chloride (BrCl) and iodine chloride (ICl) were identified as sizable peaks in the mass spectrometer, and large bursts of either compound could be observed whenever the injector was pulled back. BrCl and ICl also reacted in secondary heterogeneous reactions with

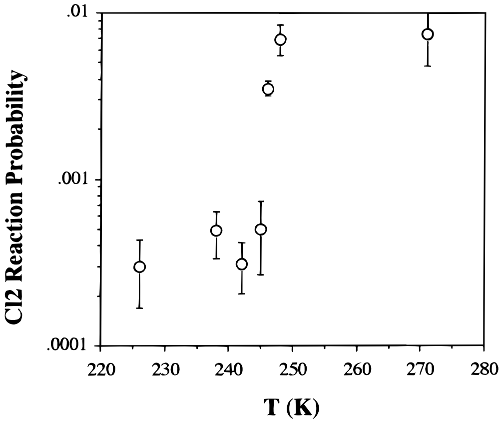

Figure 6. Uptake of Cl_2 on NaBr/ice surfaces as the system crosses its eutectic temperature at 246.1 K. Note the large change in chlorine reaction probabilities as the surface switches from a mixed solid surface of hydrated NaBr crystals and ice (T < 246.1 K) to a liquid layer of concentrated NaBr solution (T > 246.1 K). These reaction probabilities are not corrected for radial diffusion limitations. The application of such a correction, which affects high measurements most strongly, would increase the contrast between the two regimes even more.

doped ice surfaces, forming Br_2 and I_2, which were also detected as products. The same reaction of BrCl has been reported on dry NaBr salt surfaces.[15] Above the eutectic temperatures of the respective systems, BrCl and ICl could be detected only at short reaction times ($t \leq 30$ ms), indicating that liquid-phase conversion to Br_2 or I_2 was complete at longer reaction times.

The production of bromine chloride and iodine chloride in the flow tube does not, in itself, prove that these gases are necessarily products of the reactions of chlorine peroxide with bromide and iodide ions. First, excess molecular chlorine from the synthesis of chlorine peroxide comes mostly undissociated through the microwave discharge and was therefore unavoidably present in every experiment. Chlorine is known to produce BrCl upon exposure to dry NaBr salt,[15] and it is reasonable to assume that a similar reaction would occur on iodide and bromide salt hydrate surfaces:

$$Cl_2 + X^-_{(s)} \rightarrow XCl + Cl^-_{(s)} \tag{10}$$

$$XCl + X^-_{(s)} \rightarrow X_2 + Cl^-_{(s)} \tag{11}$$

In this work we observed the production of BrCl and Br_2 when NaBr/ice surfaces were exposed to chlorine. In addition, chlorine uptake rates on these bromide-doped ice surfaces (uncorrected for radial diffusion) were found to be $\gamma = (7 \pm 1) \times 10^{-3}$ in two runs at temperatures above 247 K, decreasing to only $\gamma = (4 \pm 2) \times 10^{-4}$ in four runs at temperatures of 245 K and below. This large change in Cl_2 reaction probability across the eutectic point of the NaBr/H_2O system can be clearly seen in Figure 6.

In experiments on NaI/ice surfaces, the behavior of the iodine product signals nevertheless clearly demonstrated that a reaction of chlorine peroxide produces ICl directly. In every observation of ICl^+, I_2^+, and I^+ ion signals, the ion currents rose as the microwave discharge was turned on with chlorine gases flowing. Thus, as precursor chemicals $Cl_2 + 2O_3$ are converted to $ClOOCl + 2O_2$ (with some unreacted ClO remaining), the production of iodine products increased, a difference that must be due to the reaction of chlorine peroxide, since the amount of Cl_2 present in the flow tube decreases. Although the reaction rates of Cl_2 were not measured on NaI/ice surfaces, this iodine product behavior also suggests that uptake probabilities are larger for ClOOCl than for Cl_2: although Cl_2 is present in excess, the approximately one-to-one replacement of Cl_2 by ClOOCl results in higher product yields in a time-limited flow tube measurement.

It is likely that BrCl is produced by the reaction of chlorine peroxide at NaBr/ice surfaces for two reasons. First, both Cl_2 and ICl are demonstrated to be produced by reactions of ClOOCl on ice surfaces doped with chloride and iodide ions, respectively. In addition, when Br_2 signals were monitored, the stairlike shapes of the bromine signal were similar to the chlorine peroxide signals measured immediately afterward.

The reactivity of ClOOCl on dry NaBr residue, along with the demonstration that iodine chloride is produced via a reaction of ClOOCl with NaI/ice surfaces, suggests that chlorine peroxide reacts directly with surface bromide and iodide ions. The presence of water at the surface does not appear to influence the reaction, since uptake rates were the same in similar experiments on solid NaBr/ice surfaces and on dry NaBr salt residues. The following reactions are proposed to occur:

$$ClOOCl + Br^-_{(s)} \rightarrow BrCl + products_{(s)} \tag{5b}$$

$$ClOOCl + I^-_{(s)} \rightarrow ICl + products_{(s)} \tag{5c}$$

A direct, aqueous-phase oxidation of bromide ions by ozone has been reported in the water treatment literature,[38] producing bromate with HOBr as an intermediate. The initial step in the reaction scheme is the formation of BrO^-, which can react further with O_3:

$$O_3 + Br^-_{(l)} \rightarrow O_2 + BrO^-_{(l)} \tag{12}$$

$$O_3 + BrO^-_{(l)} \rightarrow 2O_2 + Br^-_{(l)} \tag{13}$$

$$2O_3 + BrO^-_{(l)} \rightarrow 2O_2 + BrO_3^-{}_{(l)} \tag{14}$$

At no point in this scheme is Br_2 produced by the oxidation of bromide; however, HOBr (which would be in a pH-dependent equilibrium with BrO^-) might react with bromide ions and produce Br_2, as it does on ice surfaces.[43] It is known that the interconversion of bromide and BrO^- catalyzes the aqueous-phase loss of ozone.[38] To quantify the possible effects of bromide oxidation by ozone at solid NaBr/ice surfaces, ozone uptake was measured. No loss of ozone could be observed in this work while limiting injector movements to 6 cm or less; upper limits for the ozone reaction probability based on longer injector movements are the same as that for the NaCl/ice system: $\gamma \leq 5 \times 10^{-5}$ at 220 K, increasing to $\gamma \leq 2 \times 10^{-4}$ on NaBr/H_2O liquid layers above the eutectic point (270 K).

We can use this upper limit to ozone loss as a limit of oxidation of Br^- by ozone in our reaction system. At 220 K ozone is taken up by the solid NaBr/ice surface at a maximum probability of 5×10^{-5}, while ClOOCl is taken up with a reaction probability of approximately 2.5×10^{-3}. Since excess ozone was typically present in the flow tube at about 10 times the amount of ClOOCl present, the net amount of chlorine peroxide being taken up by the sodium bromide/ice surface is larger than the amount of ozone being taken up by at least a factor of 5. Therefore, if this aqueous-phase chemistry is transferable to solid NaBr/ice surfaces, we still expect that at least 5 times more bromide is oxidized via the reaction with ClOOCl (forming BrCl and then Br_2) than via reaction 14 (forming HOBr and then Br_2). Since this is an upper limit for the latter reaction, we can discount the possibility that the oxidation of bromide by ozone is primarily responsible for the production of bromine in our experiments.

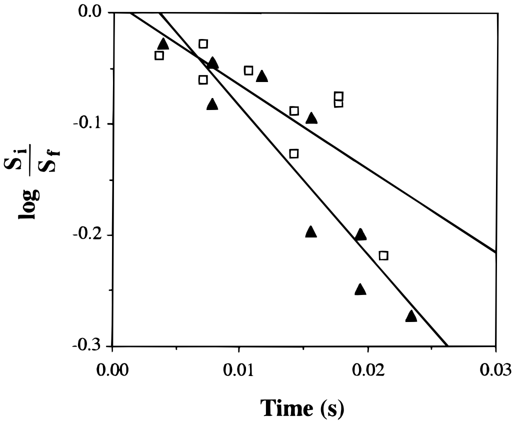

Figure 7. Sample chlorine peroxide signal losses observed due to reactions on ice and NaF/ice surfaces. Axes are defined as in Figure 2. Squares: ice surface (226 K, $\gamma = 8 \times 10^{-4}$). Triangles: HF/ice surface (217 K, $\gamma = 1.2 \times 10^{-3}$).

3.3. Reactions with HF and NaF. As expected, fluoride was the least reactive of the halides. Sample data for the loss of ClOOCl on ice and HF/ice surfaces are shown in Figure 7. Uptake of chlorine peroxide on NaF/ice surfaces was observable on six out of the seven surfaces prepared: $\gamma_{\text{avg}} = (3.1 \pm 1.5) \times 10^{-3}$ ($\pm 1\sigma$). In experiments where gaseous hydrogen fluoride was added to an ice layer already in place, most of the ClOOCl uptake rates measured (all performed with excess ClOCl present) were near the reaction detection limit; even in this data set, however, the average uptake rate was twice as fast as on pure ice surfaces and was statistically distinguishable from the latter at the 95% confidence level. It is surprising that any reaction was observed on HF/ice surfaces since HF is only a weak acid with a negligible uptake coefficient onto ice.[14] However, if the partial pressure of HF is large, HF uptake can suddenly become efficient.[14] HF/H_2O liquid layers or solid mixtures will form at the ice surface, depending on the mole fraction of HF at the surface.[44] It appears that the high HF partial pressures used in the majority of these experiments ($\geq 1 \times 10^{-3}$ Torr) were adequate to cause the formation of HF/H_2O liquid layers or solid mixtures, which were marginally reactive toward chlorine peroxide.

Small amounts of chlorine fluoride were detected during several experiments, and the signal at $m/z = 54$ sometimes behaved in the typical manner of a product (i.e., peaked as the injector was pulled back). As the injector was moved, molecular chlorine signals also displayed productlike features which were very small compared to the Cl_2 signals produced by the ClOOCl + Cl^- reaction. This small amount of molecular chlorine could be produced by heterogeneous ClOOCl decomposition, or by the following set of reactions:

$$\text{ClOOCl} + \text{F}^-_{(s)} \rightarrow \text{ClF} + \text{ClOO}^-_{(s)} \tag{5d}$$

$$\text{ClOO}^-_{(s)} \rightarrow \text{Cl}^-_{(s)} + \text{O}_2 \tag{15}$$

$$\text{ClF} + \text{Cl}^-_{(s)} \rightarrow \text{Cl}_2 + \text{F}^-_{(s)} \tag{-10}$$

The detection of ClF during ClOOCl uptake experiments on NaF/ice surfaces is an important demonstration that fluoride is reactive under these conditions, with either ClOOCl itself or with some hydrolyzed intermediate. There are no known secondary pathways to ClF formation available via reactions with either excess O_3 or Cl_2.

4. Discussion

4.1. Function of H_2O in the Reaction ClOOCl + Cl^-. The observation that ClOOCl reacts at NaCl·2H_2O/ice and HCl/ice surfaces but not at dry NaCl surfaces suggests that the reaction with chloride ions involves significant amounts of water, not necessarily acid, and is not as simple as the reactions with bromide or iodide ions. The water molecules are apparently needed to solvate one (or both) of the reactants. Instead of reacting directly with chloride (or fluoride) ions, chlorine peroxide may form a reactive hydrolyzed intermediate at the ice surface. A surface hydrolysis or ionization of ClOOCl would also explain the small interactions observed between ClOOCl and solid ice surfaces. For example, ClOOCl may be ionized before it reacts with chloride:

$$\text{ClOOCl} + \text{H}_2\text{O}_{(s)} \leftrightarrow \text{H}_2\text{OCl}^+_{(s)} + \text{ClOO}^-_{(s)} \tag{16}$$

$$\text{H}_2\text{OCl}^+_{(s)} + \text{Cl}^-_{(s)} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}_{(s)} \tag{17}$$

Infrared spectroscopic evidence for the H_2OCl^+ surface intermediate was recently found in a study of the interaction between $ClONO_2$ and ice.[45] The bonding environments of the chlorine atoms in ClOOCl and $ClONO_2$ are similar, making the molecules analogous in photolytic behavior,[46] and the polarity of the Cl−O bonds may result in similar heterogeneous reactivity for the two molecules. Another possible hydrolysis product suggested also by analogy with $ClONO_2$ is HOCl. However, a secondary reaction between HOCl and HF is thermodynamically unfavorable, calculated using either gas-phase or aqueous heats of formation.[47,48] A plausible ClOOCl hydrolysis intermediate should be reactive with both chloride and fluoride ions.

A second possibility is that chloride ions in the NaCl·2H_2O crystal may be in environments that are influenced by nearby hydrate water molecules, thereby lowering lattice energies below that of NaCl. This effect is equivalent to partial aqueous solvation and might influence surface reaction rates toward chlorine peroxide. In this case, the small uptake of (unhydrolyzed) ClOOCl observed on pure ice surfaces would be most likely due to the disproportionation of excess chlorine, which (if an analogy with aqueous-phase chemistry holds) could produce small amounts of reactive chloride ions at the ice surface:

$$\text{Cl}_2 + \text{H}_2\text{O}_{(s)} \leftrightarrow \text{HOCl} + \text{HCl}_{(s)} \tag{18}$$

$$\text{HCl}_{(s)} + \text{H}_2\text{O}_{(s)} \rightarrow \text{H}_3\text{O}^+_{(s)} + \text{Cl}^-_{(s)} \tag{19}$$

We are presently unable to distinguish between these two explanations for the function of water in the reactions of chlorine peroxide with chloride ions.

4.2. Surface Phase and Heterogeneous Reactivity. Our observations of heterogeneous reactivity are consistent with the known behavior of NaX solutions around the eutectic point. For example, the uptake of chlorine suddenly became efficient above the system eutectic point at 246 K, as shown in Figure 6. On pure ice surfaces at 183 K a negligible uptake of chlorine has been measured ($\gamma \leq 5 \times 10^{-5}$) by Kenner and co-workers.[49] Our Cl_2 uptake measurements at temperatures below the NaBr/H_2O system eutectic point were an order of magnitude larger than this, $\gamma = (4 \pm 2) \times 10^{-4}$, most likely due to the presence of NaBr salt hydrates at the ice surface. The uptake of Cl_2 into a liquid layer containing concentrated NaBr probably explains the vastly increased uptake we observed at temperatures above 246 K.

Similarly, the ClOOCl uptake probabilities shown in Figure 5 on NaBr/ice and NaI/ice surfaces shift upward at the systems' eutectic temperatures. In runs conducted on melted surfaces above the eutectic temperatures, ClOOCl reaction probabilities were near the radial diffusion limit (all $\gamma \geq 0.12$). Except for one diffusion-limited run on NaI/ice at 232 K ($\gamma \geq 0.3$), all other measured ClOOCl uptakes on solid NaBr/ice and NaI/ice surfaces were less than 0.07. These measurements imply that chlorine peroxide uptake is especially efficient into liquid layers of concentrated NaI or NaBr solutions, but also reasonably fast onto mixed solid surfaces made up of ice and hydrated NaI or NaBr crystalline phases. Although there is no dramatic shift in ClOOCl reaction probabilities on NaCl/ice surfaces at the eutectic point temperatures as there is for Cl_2 on NaBr/ice surfaces, measurements on NaCl/H_2O surfaces never exceeded the eutectic temperature, so surface melting may not have been complete.

The mechanism of deactivation of halide-doped ice surfaces toward ClOOCl reaction on a seconds-to-minutes time scale also needs to be considered. Although monolayers of ice are rapidly desorbed at the temperatures of this study,[50] we do not expect the solid salt hydrate surfaces (e.g. $NaCl{\cdot}2H_2O$) to be similarly volatile. Thus, surface saturation of the reactive sites on mixed solid NaX/ice surfaces by ClOOCl or byproducts should be possible. The perfect NaCl/ice surface renewability observed at the system eutectic point (252 K) was likely due to the presence of at least a partial surface liquid layer. Possible chemical mechanisms for deactivation of HCl/H_2O liquid layers are discussed in section 4.4.

4.3. Comparison with Chlorine Nitrate. The relative reactivity of ClOOCl with halide ions on ice surfaces, Table 2, can be compared with the heterogeneous reactivity of $ClONO_2$ with HF, HCl, and HBr. Hanson and Ravishankara[14] measured diffusion-limited losses of $ClONO_2$ on ice surfaces treated with small excess concentrations of HBr ($\gamma \geq 0.3$), but experiments where HF was added to ice layers saw essentially no losses that could be attributed to $ClONO_2$ + HF. A conservative upper limit of $\gamma = 0.01$ was put on $ClONO_2$ loss due to reaction with HF. Reaction probabilities between 0.1 and 0.3 have been measured for $ClONO_2$ + HCl on ice surfaces,[8,11] which are hardly enhanced over the fast reaction $ClONO_2 + H_2O$ on the same surface.[51] The order of halide reactivity toward $ClONO_2$ can be summarized as $Br > Cl \approx H_2O \gg F$. In our experiments, ice treated with NaF or NaCl was more reactive than undoped ice toward ClOOCl, whereas ice treated with NaBr or NaI was highly reactive. The relative order of halide reactivity toward chlorine peroxide based on these NaX/ice experiments is $I > Br > Cl \approx F > H_2O$. The main differences between $ClONO_2$ reaction kinetics and the ClOOCl + NaX/ice data presented here are the relative lack of reactivity of ClOOCl on pure ice surfaces, the relative lack of reactivity of chloride ions toward ClOOCl, and the observation of fluoride reactivity toward ClOOCl.

4.4. Possible Condensed-Phase Products. Given the general form of the reaction of chlorine peroxide with surface halide ions,

$$ClOOCl_{(g)} + X^-{}_{(c)} \xrightarrow{ice} XCl_{(g)} + products_{(c)} \qquad (5)$$

the remaining stoichiometric fragment left behind at the surface would then be the chloroperoxide ion, $ClOO^-$. Two possible reaction pathways for this ionic intermediate are suggested by the literature:

$$ClOO^-{}_{(c)} \rightarrow Cl^-{}_{(c)} + O_2 \qquad (15)$$

$$ClOO^-{}_{(c)} + H_3O^+{}_{(c)} \leftrightarrow HOOCl_{(c)} + H_2O_{(c)} \qquad (20)$$

The unimolecular decomposition was postulated as a liquid-phase reaction by Khan and Kasha,[52] while protonation would form HOOCl, the product suggested by Wofsy et al.[6] We speculate that the unimolecular decomposition may occur on any type of surface, but the formation of HOOCl is restricted to acidic surfaces (e.g. HCl/H_2O liquid layers). Efforts to identify either HOOCl or O_2 as gas-phase products in the mass spectrometer were not successful. Direct surface analysis techniques are needed to provide evidence for the formation of $ClOO^-$ and HOOCl.

In early studies of the aqueous-phase Cl_2 + HOOH reaction system, HOOCl was postulated as an intermediate.[53,54] The formation of HOOCl explained both the kinetics of the disappearance of reactants[53] and the observed preservation of both oxygen molecules from HOOH in the O_2 produced (in O^{18} tracer experiments).[54] In this mechanism, once HOOCl is formed, it reacts via one of two pathways:

$$HOOCl_{(l)} \rightarrow O_{2(g)} + H^+{}_{(l)} + Cl^-{}_{(l)} \qquad (21)$$

$$HOOCl_{(l)} + H^+{}_{(l)} + Cl^-{}_{(l)} \leftrightarrow Cl_{2(g)} + HOOH_{(l)} \qquad (22)$$

If this reaction mechanism is correct, and if the rate of reaction 22 is comparable to that of reaction 21 in fairly concentrated HCl solutions, it could explain the deactivation of HCl/H_2O liquid layers observed in our experiments. Decomposition of HOOCl into H^+, Cl^-, and O_2 in the surface HCl/H_2O liquid layer replenishes the reactive chloride ion (and is equivalent to reaction 15), but the reaction of HOOCl with HCl removes chloride ions from the liquid layer, thus deactivating it toward further reaction with ClOOCl. Thus, while the identity of any condensed-phase products of heterogeneous chlorine peroxide reactions remains speculative, our qualitative observations of surface deactivation patterns on NaCl/ice and HCl/ice surfaces are at least compatible with the formation of HOOCl in HCl/H_2O liquid layers.

5. Conclusion

These discharge flow/mass spectrometric studies provide the first experimental evidence of heterogeneous reactions between chlorine peroxide and all four halide ions at ice surfaces. The mixed halogen gases XCl, where X = I, Br, Cl, and F, were the only gas-phase products observed during ClOOCl uptake experiments on ice surfaces doped with either NaX or HX.

Liquid layers formed at the surface of HCl/ice coatings used in this study because of high concentrations (0.004−0.06 Torr) of gas-phase HCl. Similarly, liquid layers may have formed at the surface of ice layers treated with gaseous HF. Liquid layers also presumably formed at the surface of NaX/ice coatings, but only in the few runs performed above the temperature of the eutectic point of the respective system (where ice, hydrated NaX crystals, and NaX solution coexist). Below the eutectic temperature, only ice and hydrated NaX crystals are thermodynamically stable; thus, the reaction surfaces consisted of a mixture of these two solids. Measurements both above and below the eutectic temperatures were made on NaI/H_2O and NaBr/H_2O systems. Molecular chlorine reaction probabilities on NaBr/ice surfaces were greatly increased, while ClOOCl reaction probabilities on both types of surfaces were slightly increased, as the transition was made from solid to liquid-phase reaction surfaces.

Chlorine peroxide uptake was rapid on solid NaI/ice and NaBr/ice surfaces and on dry NaBr salt residue. On ice surfaces doped with NaCl, HCl, or NaF, reactive uptake was slower, but still significantly above the small observed uptake on pure ice surfaces, as summarized in Table 2. No ClOOCl uptake was observed on dry NaCl residue, suggesting that the presence of water is needed to solvate one of the reactants. ClOOCl reaction probabilities measured on (liquid) HCl/ice surfaces were as high as $\gamma = 0.0065$.

On the basis of this work we cannot reliably predict the uptake probability for ClOOCl on PSC particles under stratospheric conditions. First of all, if surface deactivation of NaCl/ice surfaces is caused by saturation of reactive sites by ClOOCl or by reaction products, the uptake probability of ClOOCl onto NaCl/ice surfaces may increase if chlorine peroxide concentrations are reduced to typical stratospheric levels. Second, the solid NaCl/ice surfaces contained mixed $NaCl{\cdot}2H_2O$ and ice phases with unknown surface coverages. Most importantly, our solid NaX/ice and liquid HCl/H_2O reaction surfaces are probably significantly different from the surfaces of real PSC particles. These particles exist in an environment where HCl concentrations are orders of magnitude lower than concentrations over our bulk HCl/ice surfaces. These low amounts of HCl are not sufficient to form a thermodynamically stable surface liquid layer on solid particles, but may form only a thin, quasi-liquid layer of ionized HCl.[17,55,56]

Trajectory modeling studies of the Arctic stratosphere[5] have indicated that the reaction $ClOOCl + Cl^- \rightarrow Cl_2 +$ products could have a significant effect on chlorine activation and ozone depletion rates if HOOCl is formed (with subsequent photolysis or further reaction with HCl) and if chlorine peroxide's reaction probability on PSC surfaces is greater than 0.03. Although the current study does not demonstrate that these two conditions are met, potential stratospheric significance for the heterogeneous reactions of chlorine peroxide with halide ions should not yet be ruled out. HOOCl was not observed in this work, but its formation in HCl/H_2O liquid layers is consistent with observed patterns of surface deactivation toward ClOOCl uptake. The reaction probability for chlorine peroxide on stratospheric particles cannot yet be estimated. Clearly, measurements conducted under stratospheric conditions and the direct detection of condensed-phase products are urgently needed to address the role of heterogeneous ClOOCl chemistry in the stratosphere.

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Registry No.: ClOOCl, 12292-23-8; NaI, 7681-82-5; NaBr, 7647-15-6; NaCl, 7647-14-5; HCl, 7647-01-0; NaF, 7681-49-4; HF, 7664-39-3; NaOCl, 7681-52-9; H_2O, 7732-18-5.

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