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Kinetics and Product Yields in the Heterogeneous Reactions of HOBr with Ice Surfaces Containing NaBr and NaCl

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The heterogeneous reactions of HOBr with ice surfaces formed by freezing sodium halide solutions were studied using a coated-wall, low-pressure flow tube coupled to a quadrupole mass spectrometer. Experiments were conducted at 233 and 248 K with films containing bromide, chloride, or a mixture of the two, and with HOBr gas-phase concentrations of about 10^{12} molecules/cm^3. Gas−surface uptake coefficients and product yields are presented for a range of halide and hydrogen ion concentrations. Compared to analogous reactions with HOCl, HOBr reactions were slower than expected with a maximum uptake coefficient of approximately 0.01. At both 233 and 248 K, gas-phase Br_2 was formed exclusively from bromide-only films and only BrCl was formed from chloride films. When both ions were present, BrCl was the sole gas-phase product observed at 233 K, while both gas-phase Br_2 and BrCl were formed at 248 K. The relative yields of the gas-phase products depend on the temperature, composition, and acidity of halide-ice surfaces. A mechanism consistent with the observations involves initial formation of a $HOBr{\cdot}X^-$ complex, where X^- is either chloride or bromide, followed by reaction of the complex with a proton. For this reason, reaction probabilities for the formation of BrCl or Br_2 were higher on acidified films than on films formed from pH-neutral solutions. The atmospheric implications of these results are discussed.

Introduction

Almost complete loss of O_3 is frequently observed in stable boundary layer air in the springtime Arctic.[1−3] Low O_3 mixing ratios are correlated with high concentrations of bromine compounds collected on filters, suggesting that elevated levels of brominated species such as Br, HBr, and HOBr are formed during ozone loss events.[1−3] Measurements of light nonmethane hydrocarbons have confirmed the presence of bromine atoms and indicated that chlorine atom concentrations are also elevated during low-ozone periods.[4] The hydrocarbon analyses imply that there are large numbers of active halogen compounds in the Arctic boundary layer; these molecules photolyze after polar sunrise, releasing Br and Cl atoms that react with hydrocarbons and ozone. Recent measurements have confirmed the existence of tens of parts per trillion of Br and Cl atom precursors such as Br_2,[5,6] BrCl,[5] HOBr, Cl_2, and HOCl[6] during episodes of O_3 destruction. In addition, satellite measurements show that BrO mixing ratios are elevated in areas where O_3 depletion occurs.[7,8] On the basis of these observations, it is thought that ozone loss occurs via a catalytic cycle involving Br and BrO:

$$2[Br + O_3 \rightarrow BrO + O_2] \tag{R1}$$

$$BrO + BrO \rightarrow Br_2 + O_2 \tag{R2}$$

$$Br_2 + h\nu \rightarrow 2Br \tag{R3}$$

$$\text{Net:}\ Br_2 + 2O_3 \rightarrow 2Br + 3O_2$$

Formation of HBr can terminate this catalytic cycle through reaction of Br atoms with hydroperoxyl radical (HO_2) or oxygenated organic compounds such as formaldehyde and acetaldehyde:[9]

$$Br + HO_2 \rightarrow HBr + O_2 \tag{R4}$$

$$Br + HCHO \rightarrow HBr + HCO \tag{R5}$$

$$Br + CH_3CHO \rightarrow HBr + CH_3CO \tag{R6}$$

The removal of BrO may also limit ozone destruction via formation of HOBr:

$$BrO + HO_2 \rightarrow HOBr + O_2 \tag{R7}$$

HBr and HOBr are stable, nonradical reservoir species that secure bromine in forms unreactive to O_3. Because the observed Arctic O_3 loss occurs on a very short time scale, mechanisms must exist for conversion of reservoir bromine back into photochemically active compounds. HOBr molecules may photolyze directly to release Br and OH.[10] Alternatively, HOBr and HBr may recycle into gas-phase Br_2 via aqueous-phase interactions with sulfate aerosol particles:[11,12]

$$HBr \rightarrow H^+ + Br^- \tag{R8}$$

$$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O \tag{R9}$$

Aqueous Br_2 formed in (R9) rapidly degasses into the atmosphere. Subsequently, gas-phase Br_2 can photolyze to Br atoms that may destroy O_3 via (R1).

There is some question as to the source and identity of the halogen compounds responsible for initiating the O_3 loss. Recent modeling studies have focused on the large amounts of active bromine that may be quickly introduced into the troposphere by reactions on the surfaces of sea salt aerosols, snow, or sea

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ice.[13−18] An autocatalytic cycle explains many aspects of the rapid loss of ozone seen in the Arctic:[15]

Condensed-phase surface reactions

$$HOBr + Cl^- + H^+ \leftrightarrow BrCl + H_2O \qquad (R10)$$

$$BrCl + Br^- \leftrightarrow Br_2Cl^- \qquad (R11)$$

$$Br_2Cl^- \leftrightarrow Br_2 + Cl^- \qquad (R12)$$

Gas-phase atmospheric reactions

$$Br_2 + h\nu \rightarrow 2Br \qquad (R3)$$

$$2[Br + O_3 \rightarrow BrO + O_2] \qquad (R1)$$

$$2[BrO + HO_2 \rightarrow HOBr + O_2] \qquad (R7)$$

$$\text{Net: } Br^- + 2O_3 + H^+ + 2HO_2 + h\nu \rightarrow HOBr + 4O_2 + H_2O$$

This reaction chain has the potential to convert large amounts of sea salt bromide into the photochemically active molecules Br_2 and BrCl. The cycle continues until BrO concentrations are high enough that step R2 becomes competitive with (R7), and catalytic O_3 loss ensues.

Instead of occurring on sea salt aerosol, the heterogeneous chemistry may also take place on ice surfaces in the Arctic snowpack.[16,17] Thus, a majority of the gas-phase Br_2 and BrCl present at polar sunrise[5] may be released from sea salt bromide accumulated on surface snow and coastal sea ice. A recent modeling study reports that tropospheric O_3 depletion cannot be simulated in accordance with field observations unless halogen reactions occurring in the Arctic snowpack are included.[18]

Most previous laboratory studies of heterogeneous ice reactions were performed at very low temperatures, to investigate polar stratospheric cloud chemistry. Kirchner and co-workers were the first to experimentally confirm release of gas-phase Br_2 and BrCl from the transport of HOBr over sea salt-doped ice at 230−240 K, but they only reported kinetic data for reactions on ice surfaces containing 18% chloride, 23% bromide, and 18% chloride with 0.06% bromide.[19] Abbatt found that HOBr and HBr react together on ice at 228 K to produce Br_2 and BrCl.[20] In a similar study, Chu and Chu observed formation of BrCl in the reaction of HOBr and HCl on ice at 190−222 K.[21] Oum et al. reported formation of gas-phase Br_2 from the reaction of seawater ice with ozone in the dark.[22] Waschewsky and Abbatt studied the solubility of HOBr and its reaction with HCl in sulfuric acid solutions as a proxy for aqueous-phase chemistry on sulfate aerosols.[23] Abbatt and Waschewsky also examined the interactions of HOBr, HNO_3, and NO_2 on deliquescent NaCl aerosols, which they used as surrogates for marine aerosols.[24] Fickert and associates have published a comprehensive investigation of the uptake of HOBr by aqueous salt solutions.[25] They observed formation of gas-phase Br_2 and BrCl and found the relative ratio of the products depends on the acidity and halide content of the salt solutions. Most recently, a study of HOBr interacting with simulated sea ice surfaces similar to those used in this work has been published by Adams et al.[26]

Motivated by the potential significance of reactions occurring on sea ice, we have undertaken studies of the interactions of various atmospheric trace gases with ice surfaces containing bromide and chloride ions. Previously, we reported significant gas-phase Br_2 production from the heterogeneous reactions of Cl_2 and HOCl with simulated sea ice surfaces.[27] Here we present results from studies of the interaction of HOBr with ice films containing sodium halide ions. Both gas-phase Br_2 and BrCl are formed as products, in yields that are sensitive to the temperature and composition of the halide-ice surfaces. Due to the shortage of relevant data describing the reactions of HOBr with chloride and bromide in ice, most current models describing tropospheric O_3 depletion incorporate kinetic values extrapolated from analogous aqueous-phase chemistry.[28,29] We find evidence that this approach is not necessarily valid.

Experimental Section

Experiments were conducted in a low-pressure flow tube coupled to an electron-impact quadrupole mass spectrometer using an approach fully described in previous publications.[12,23,27,30] Here we outline the technique and describe aspects of the methodology pertinent to this work. Experiments were designed to measure the kinetic parameters and product formation in the heterogeneous ice reactions of HOBr, (R9) and (R10), potentially important in the boundary layer. Because temperatures at polar sunrise are between 230 and 250 K, we ran experiments at 233 and 248 K to match the range of conditions in the Arctic springtime.

To measure the product yields of (R9), it was necessary to synthesize HOBr without excess Br_2. And so, HOBr was generated using[31]

$$AgNO_3 + H_2O + Br_2(aq) \rightarrow HOBr(aq) + AgBr(s) + HNO_3(aq) \qquad (R13)$$

Over 45 min, 5 mL of Br_2 was added to a solution of 24.5 g of $AgNO_3$ in 150 mL of water. Aqueous HOBr was isolated by vacuum distillation for 2−4 h, and 20 mL of 20% sulfuric acid was added to the distillate. To remove traces of Br_2, HOBr was purified by bubbling UHP helium through the solution for 5 min. The product was a pale yellow aqueous HOBr solution that was stable for about 3 weeks when stored in the dark at 0 °C. During experiments, gaseous HOBr was introduced into the flow tube by bubbling UHP helium through an aqueous HOBr solution at a rate of 10−20 standard cubic centimeters per minute (sccm). Data in Figures 1−4 demonstrate that the Br_2 mass spectrometer signal was approximately 10−40% that of the HOBr signal. All experiments were performed with HOBr concentrations maintained at $(1 \pm 0.3) \times 10^{12}$ molecules cm^{-3} in the flow tube, as determined by absorbance measurements of the HOBr flow at 280 nm.

HOBr reactions were investigated on films containing only bromide, only chloride, or a mixture of chloride and bromide ions. Halide-ice films were made by coating the inner wall of a 2.34 cm i.d. Pyrex reaction tube with 1 mL of aqueous sodium halide solution. Tables 1 and 2 give the range of halide concentrations used. Experiments were conducted on single component films to gauge the influence of temperature, halide concentration and acidity on the chemistry. To better represent sea ice, we used films containing both chloride and bromide ions in the ratios found in natural seawater. Two different concentrations of chloride/bromide mixed films were made in order to mimic the variation of halide concentrations in Arctic sea ice. It is likely that a range of halide concentrations are present on natural ice surfaces due to enhancement from the freezing process and by deposition of sea salt aerosols, which

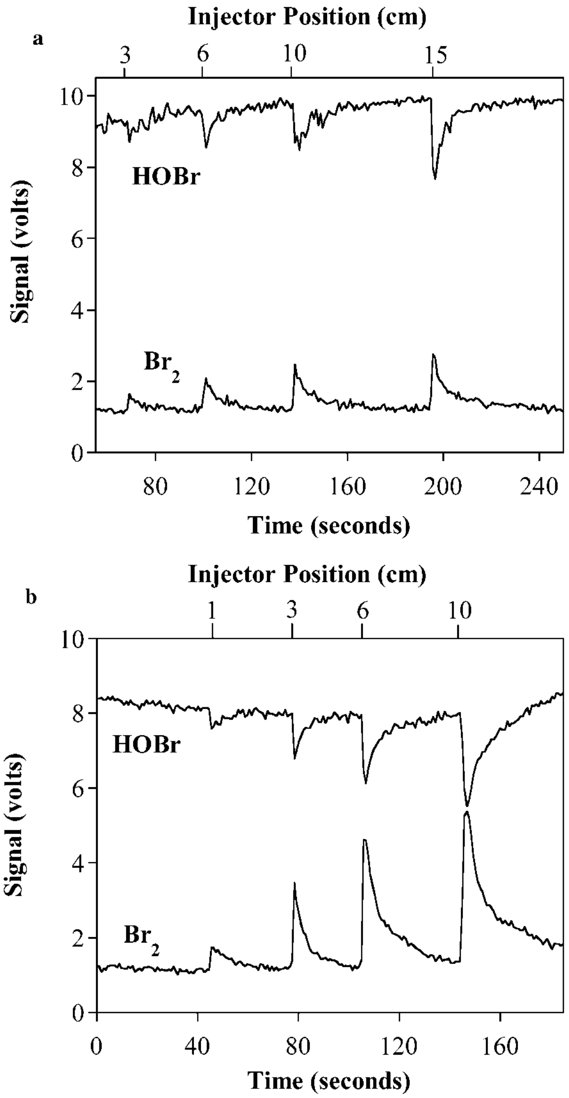

Figure 1. Representative data for the reaction of HOBr with a pH 2 film containing 0.08 wt % bromide at (a) 233 K and (b) 248 K.

become enriched in chloride and bromide at relative humidities below 100%.

For each halide concentration, the acidity of the ice was varied. Hydrogen ion concentrations were raised by adding sulfuric acid to the halide solutions from which the films were made. The final solution pH was made by a pH meter measurement. In this paper, we use the "pH of the ice surface" as a way to express the hydrogen ion content of halide-ice films, even though the surface may have had a different pH than the bulk. We refer to the ice surfaces as "halide-ice films" or "halide surfaces", even though the films also contained hydrogen ions.

After being coated with solution, the reaction tube was inserted into a cold flow tube. This created a halide-ice film that was less than 0.1 mm thick and transparent. When using pure water, we know that these films are much smoother than vapor-deposited films.[32] We assume the same is true for relatively dilute salt solutions. To prevent net evaporation of the ice film, water vapor was added to the reaction tube by bubbling a flow of UHP helium through a water trap. Water partial pressures were kept within 10% of the vapor pressure of the ice film. UHP helium was used as carrier gas, and total flow rates were 320−330 sccm for experiments at 233 K and 190−200 sccm for experiments at 248 K. Flow tube pressures were 0.8 Torr at 233 K and 2 Torr at 248 K.

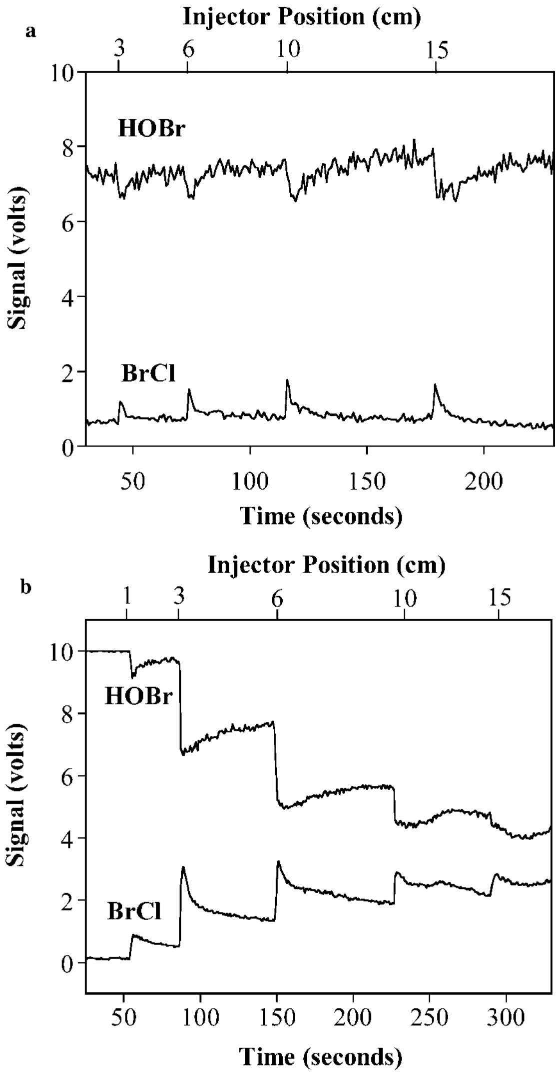

Figure 2. Representative data for the reaction of HOBr with a pH 2 film containing 23 wt % chloride at (a) 233 K and (b) 248 K.

Kinetics experiments were initiated by establishing a flow of gaseous HOBr through a moveable glass injector that was pushed into the flow tube past the end of the film. When the HOBr mass spectrometer signal was steady, a portion of the film was exposed to the reactant gas by pulling the injector back a few centimeters over a period of 1−2 s. HOBr, BrCl, and Br_2 were measured as parent ions at masses 96, 116, and 160, respectively.

Gas−surface uptake coefficients (γ) were calculated from first-order rate constants measured for the loss of HOBr on the wall surface. The rate constants were extracted by monitoring the drop in HOBr signal as a function of the length of fresh halide-ice surface that was exposed by the moveable injector.[33] When reaction of HOBr with a halide-ice film is very fast, the overall loss rate of HOBr is limited by its ability to diffuse through the helium−water carrier gas to the reactive walls of the flow tube. To account for this, a diffusion correction was applied to the observed first order decays[34] using diffusion coefficients calculated for a helium−water gas mixture.[35] Due mainly to variations in ice surfaces from experiment to experiment, the major uncertainty arises from scatter in the individual uptake coefficient values. To maximize the precision of the data, each reported uptake coefficient is the mean of 2−9 experimental results.

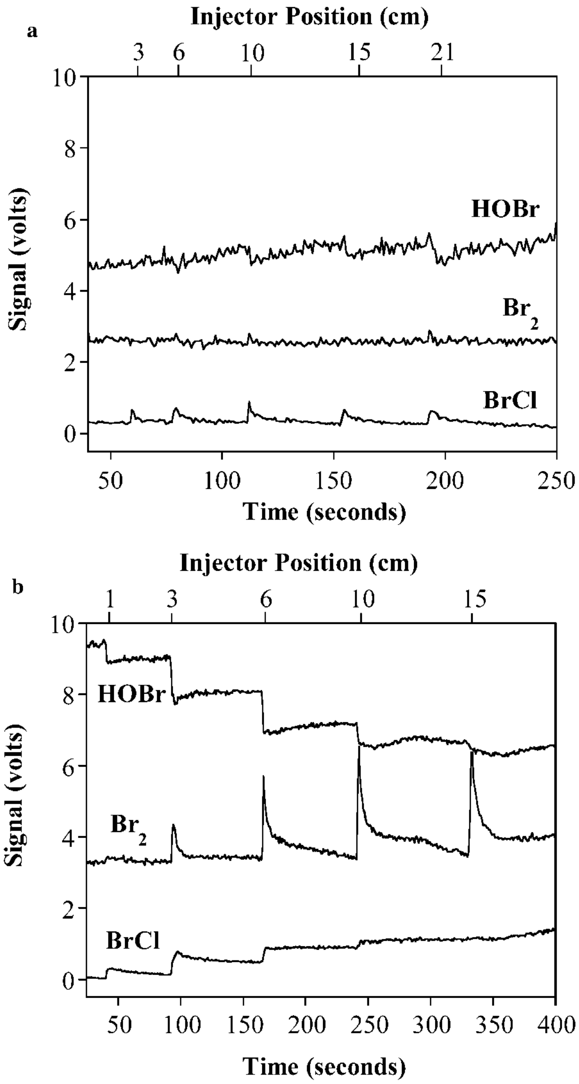

Figure 3. Representative data for the reaction of HOBr with a pH 2 film containing 23 wt % chloride and 0.08 wt % bromide at (a) 233 K and (b) 248 K. In Figure 3b, the HOBr signal has been offset 4.5 V for clarity.

To determine product yields, HOBr, Br_2, and BrCl mass spectrometer signals were correlated with their gas-phase concentrations in the flow tube. The calibration ratio for HOBr was established by relating its flow tube concentration, determined by absorbance at 280 nm, with its mass spectrometer signal. To calibrate Br_2 and BrCl, a dilute mixture of the gases was prepared in UHP helium.[27] Br_2 and BrCl signals were calibrated using flow tube concentrations calculated from the pressure drop with time of the reservoir containing the He−BrCl−Br_2 mixture. Calibration ratios were used to estimate the amount of HOBr reacted and Br_2 and/or BrCl formed as the moveable injector was pulled back a specific distance. At 233 K, product yields were calculated from data when the injector was moved from 6 to 10 cm, whereas at 248 K data from 1 to 3 cm were used The reported product yields are the average values for all experiments performed.

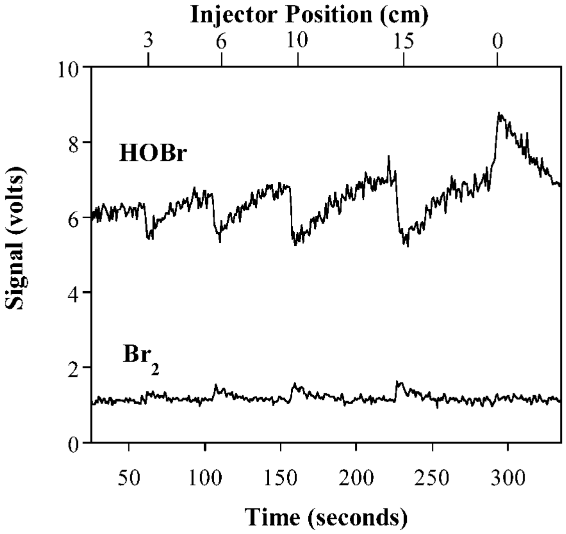

Figure 4. An example of a surge in HOBr signal above its original steady-state level when the injector was pushed back in at the conclusion of the experiment (i.e., at 0 cm). These data are from the reaction of HOBr with a pH 6 film containing 0.08% bromide at 233 K.

TABLE 1: Uptake Coefficients and Product Yields for Reactions at 233 K[a]

wt %				yield (%)			
$[Br^-]$	$[Cl^-]$	pH	HOBr uptake coeff ($\times 10^{-3}$)[b]	Br_2	BrCl	reacn prob[c] ($\times 10^{-3}$)[b]	N[d]
5		6	8.2 ± 1.9	26 ± 5		2.1 ± 0.6	3
		2	11 ± 3	15 ± 2		1.7 ± 0.5	6
0.8		6	12 ± 3	11 ± 2		1.3 ± 0.4	5
		2	12 ± 2	16 ± 3		1.9 ± 0.5	6
0.08		6	9.3 ± 2.5	9 ± 2		0.86 ± 0.30	8
		2	8.2 ± 1.1	17 ± 5		1.4 ± 0.5	6
		1.5	10 ± 3	23 ± 3		2.3 ± 0.8	4
0.02		6	4.4 ± 1.0	13 ± 6		0.57 ± 0.29	4
		2	6.0 ± 1.7	43 ± 17		2.6 ± 1.2	5
0.008		6	4.8 ± 1.7	12 ± 5		0.58 ± 0.32	9
		2	2.7 ± 1.2	35 ± 16		0.95 ± 0.60	5
	23	6	1.8 ± 0.4		4.9 ± 1.2	0.09 ± 0.03	5
		2	3.8 ± 0.5		16 ± 4	0.61 ± 0.17	4
		1.5	3.2 ± 0.6		44 ± 16	1.4 ± 0.6	5
	2.3	6	1.7 ± 0.6		5.1 ± 1.8	0.09 ± 0.05	5
		2	4.9 ± 1.1		17 ± 2	0.83 ± 0.21	4
0.08	23	6	1.0 ± 0.3		7.1 ± 2.0	0.07 ± 0.03	4
		2	1.6 ± 0.2		9.9 ± 2.7	0.16 ± 0.05	3

[a] Reported values are averages of the number of experiments listed, and uncertainties are $1 - \sigma$ precisions. [b] Entries in the table should be multiplied by 10^{-3}. [c] Reaction probability = (uptake coefficient)(product yield). [d] Number of experiments.

Results

Experiments at 233 K. Table 1 lists results for 233 K, and Figures 1a, 2a, and 3a contain representative data for heterogeneous reactions of HOBr with a 0.08% bromide film, a 23% chloride film, and a 23% chloride/0.08% bromide mixed film, respectively, where "%" refers to percentage by weight. Note that the reaction probability is calculated by multiplying the observed HOBr uptake coefficient by the product yield. In the figures, reactant and product mass spectrometer signals are plotted versus both experiment time and moveable injector position. The injector was pulled out incrementally during the course of an experiment, exposing increasingly larger sections of fresh halide-ice film to HOBr. Typically, the injector was moved to positions of 1, 3, 6, 10, and 15 cm, which revealed 1, 2, 3, 4, and 5 cm sections of unreacted halide-ice surface, respectively. This procedure is slightly different from that used in standard uptake studies because reactive halide and hydrogen ions were consumed during the course of an experiment. For example, in Figure 1a the injector was moved at 60 s from 1 to 3 cm, exposing 2 cm of fresh bromide-ice surface. The HOBr signal dipped slightly and the Br_2 signal peaked as HOBr reacted with Br^- and H^+ on the ice-coated wall, producing gas-phase Br_2. Control experiments showed that uptake of HOBr onto pure

TABLE 2: Uptake Coefficients and Product Yields for Reactions at 248 K[a]

wt %			HOBr uptake	yield (%)		reacn prob ($\times 10^{-3}$)[b]		
[Br$^-$]	[Cl$^-$]	pH	coeff ($\times 10^{-3}$)[b]	Br_2	BrCl	Br_2[c]	BrCl[d]	N[e]
0.08		6	2.3 ± 0.6	30 ± 5		0.7 ± 0.2		4
		2	5.8 ± 0.3	39 ± 2		2.2 ± 0.2		4
		1.5	6.7 ± 1.0	34 ± 5		2.3 ± 0.5		5
	23	6	13 ± 4		4.6 ± 0.4		0.65 ± 0.24	4
		2	17 ± 4		10 ± 2		1.7 ± 0.5	4
0.08	23	6	17 ± 7	7 ± 1	3.6 ± 0.8	1.2 ± 0.5	0.68 ± 0.33	4
		2	13 ± 3	18 ± 5	7.9 ± 1.1	2.3 ± 0.8	1.0 ± 0.3	4
0.008	2.3	6	4.1 ± 0.6		5.1 ± 0.5		0.21 ± 0.05	2
		2	6.8 ± 0.2	7.4 ± 2.5	13 ± 0	0.5 ± 0.2	0.88 ± 0.03	2

[a] Reported values are averages of the number of experiments listed, and uncertainties are $1 - \sigma$ precisions. [b] Entries in the table should be multiplied by 10^{-3}. [c] Br_2 reaction probability = (HOBr uptake coefficient)(Br_2 product yield). [d] BrCl reaction probability = (HOBr uptake coefficient)(BrCl product yield). [e] Number of experiments.

ice is negligible compared to the loss observed with the sodium halide/ice films. Consequently, HOBr and Br_2 signals decayed back to their original values in a time-dependent manner as bromide and hydrogen ions on the ice surface were reacted away. Then, the injector was moved from 3 to 6 cm at 100 s, from 6 to 10 cm at 140 s, and from 10 to 15 cm at 195 s. Each time the injector was pulled back, the HOBr signal dropped somewhat lower and the Br_2 signal rose higher than before because progressively greater amounts of reactive ions were available in successively longer portions of fresh ice film.

Table 1 shows that there is a tendency toward higher reaction probabilities with increasing acidity for all films studied, except for the most concentrated bromide film. In addition, for the single component bromide films, reaction probabilities rise with bromide concentrations in the ice film for the pH 6 films but not for pH 2. A similar relationship was not observed for reactions on chloride films, perhaps because only concentrated films were studied.

Halide film acidity is correlated with product yields for almost all the films. This trend is particularly evident for chloride films and dilute bromide films, where there are noticeable enhancements in gas-phase products at pH 2 and/or pH 1.5. No connection between halide concentrations and product yields was observed. Reactions with bromide surfaces produced only Br_2, as seen in Figure 1a. Similarly, Figure 2a demonstrates that reaction of HOBr with chloride films released only BrCl. These products were anticipated on the basis of the chemistry of HOBr shown in (R9) and (R10). HOBr was observed to react solely with chloride in 23% chloride/0.08% bromide mixed films, as indicated by BrCl production and no formation of Br_2 (Figure 3a). This result was unexpected because bromide concentration in the mixed film was sufficient for reaction to occur in the single component 0.08% bromide film, with $\gamma \cong$ 0.01.

When the movable injector was pushed back in at the conclusion of most experiments, we saw a momentary surge in the HOBr signal above its original steady-state level, as shown in Figure 4. Surges in HOBr signals were observed in experiments using every type of film listed in Tables 1 and 2 except those with very low halide concentrations, specifically 0.02% and 0.008% bromide films. A surge of this type is typically due to desorption of gas-phase molecules that have been taken up by the surface. Abbatt did not see any evidence for this kind of reversible adsorption of HOBr onto a pure ice surface at 228 K,[20] nor did we detect any reversible uptake when HOBr was exposed to an ice film that did not contain halide ions.

Experiments at 248 K. Table 2 lists results for 248 K, and Figures 1b, 2b, and 3b show representative data for reactions of HOBr with a 0.08% bromide film, a 23% chloride film, and a 23% chloride/0.08% bromide mixed film, respectively. The uptake coefficients were calculated in the manner described above, using the rapid decline observed after exposure to increasingly longer distances of unexposed surface.

Data in Figures 2b and 3b lie in sharp contrast to those in Figures 2a and 3a. In experiments with the chloride and mixed bromide/chloride films, HOBr and BrCl signals did not recover to their initial values after the injector was pulled out. This effect was particularly noticeable as longer amounts of surface were exposed. At a certain point, HOBr and BrCl signals essentially leveled off, as shown at injector positions of 10−15 cm in Figures 2b and 3b. Data of this sort are commonly the signature of chemistry occurring on a surface containing a solution because liquid components do not become depleted at the reactive interface as rapidly as in solid surface reactions. Reactive components are mobile in the liquid phase and can migrate to the reactive interface, unlike in the solid phase where diffusion times are slow. Following this reasoning, data in Figures 2b and 3b suggest that 23% chloride films and chloride/bromide mixed films contained liquid to some degree at 248 K.

Results in Table 2 show that there is a tendency toward larger reaction probability values and higher product yields in reactions with films containing more hydrogen ions. As at 233 K, Figures 1b and 2b indicate the sole product from reactions with bromide films was Br_2, and only BrCl was released in reactions with chloride films. For experiments with chloride/bromide mixed films, a significant change at 248 K is that gas-phase Br_2 and BrCl were both produced, as shown in Figure 3b. Uptake coefficient values for 23% chloride/0.08% bromide are about 10 times greater at 248 K than at 233 K.

Discussion

Experiments at 233 K. We first develop a reaction mechanism consistent with the data in Table 1 for the pure bromide and chloride systems and then briefly discuss the results for the mixed-halide films. The mechanism must be able to explain the following: (1) the upper limit to the uptake coefficient of roughly 0.01 for the bromide films, (2) the dependence of the reaction probability for Br_2 formation on the bromide concentration of the pH 6 bromide films, (3) the enhancement in the reaction probabilities as the pH was lowered from 6 to 2 in almost all cases, (4) the independence of the product yields on the acidity, (5) product yields less than 100%, and (6) reversible HOBr desorption on halide-containing films.

Without detailed knowledge of how the film surface composition depends on the bulk composition, we present only a qualitative model. In particular, as shown in Figure 5, we consider a Langmuir−Hinshelwood type surface mechanism.

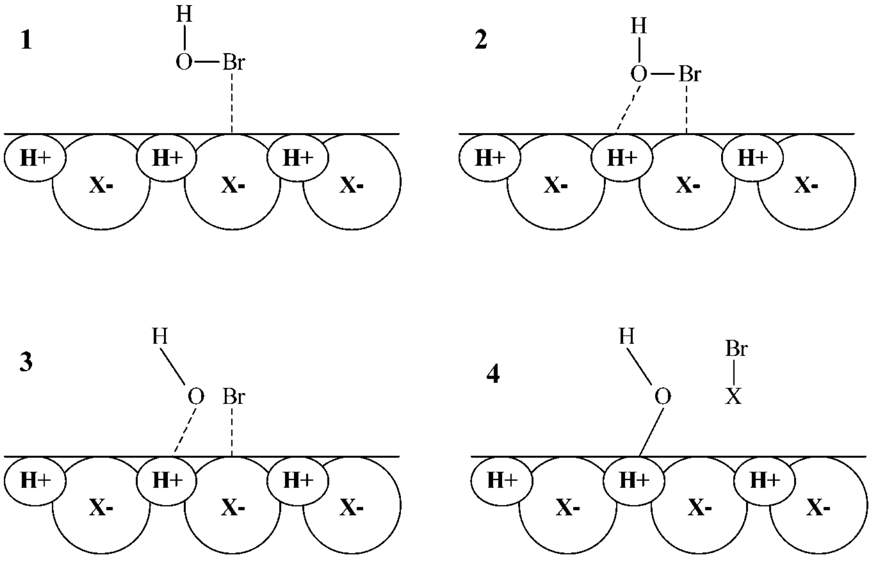

Figure 5. Schematic depiction of a Langmuir−Hinshelwood type surface mechanism for reaction of gaseous HOBr with X^- (where X^- represents Cl^- or Br^-) on the surface of a halide-ice film. Step 1 is reversible binding of gas-phase HOBr to a halide ion on the ice surface. Step 2 represents the transition state, where the oxygen-portion of the HOBr ionic adduct binds to a hydrogen ion on the ice surface. Step 3 is formation of reaction products H_2O and BrX, which are bound to the ice surface. Step 4 involves release of the bound product BrX into the gas phase.

The reaction proceeds when the $Br^{\delta+}$ end of a gaseous HOBr molecule binds to a halide ion on the ice surface and forms an ionic adduct. Support for this step comes from our observation of reversible uptake of HOBr to halide-ice surfaces, a process does not occur to a similar degree on a pure ice surface. Integration of the desorption peak,[36,37] indicates that $(2 \pm 1) \times 10^{14}$ molecules of HOBr per cm^2 had reversibly adsorbed to the film, where the geometric surface area has been used. In previous work, the same uptake was measured for the adsorption of HNO_3 to ice to yield a saturated surface coverage.[37] The inference is that close to a monolayer of HOBr exists on the surface of our more concentrated halide−ice films for the HOBr partial pressures employed. The size of the desorption peak was somewhat smaller for the more dilute films (0.008−0.02 wt % bromide) presumably because the anion coverage on the film surfaces was lower.

Ab initio calculations indicate that $HOBr{\cdot}Br^-$ and $HOBr{\cdot}Cl^-$ anionic complexes are stable with large binding energies of 17.7 and 21.5 kcal mol^{-1}, respectively.[38] Although these are gas-phase binding energies that will be somewhat different from those prevalent on an ice surface, they nevertheless suggest that this is a likely first step in the reaction pathway. Subsequently, the $O^{\delta-}$ portion of the adduct interacts with a hydrogen ion on the ice surface, forming the transition state. The reaction can proceed forward to the third step, where the bond between Br and O in the original HOBr molecule breaks, leaving H_2O and either Br_2 or BrCl adsorbed on the ice surface. The last step is release of Br_2 or BrCl into the gas phase.

This mechanism explains many of the relationships in the data that we have noted. Reaction probability values listed in Table 1 at pH 6 increase with increasing bromide concentrations because more HOBr molecules can bind to the bromide-ice surface when additional bromide ion binding sites are available. This relationship may not have been observed for chloride films because ice surfaces were completely covered with chloride ions for both salt concentrations used. A similar result was observed for the reaction of Cl_2 with concentrated bromide-ice surfaces at 233 K, and it was determined that ice surfaces were saturated with bromide ions at concentrations of approximately 3% and greater.[27] In this regime, increasing the bromide concentration in the ice film beyond ∼3% did not increase the uptake coefficient. The fact that no increase in uptake coefficient was observed for the chloride films, despite an order of magnitude increase in chloride concentration, suggests that the ice surface was saturated at chloride concentrations of 2.3%. It is possible that the 5% bromide film was also saturated.

The correlation between acidity and both higher product yields and reaction probabilities is also consistent with the mechanism. Because H^+ is required for product formation in (R9) and (R10), higher product yields and faster kinetics result from reactions with halide-ice films containing elevated concentrations of hydrogen ions. The reverse relationship is also true: product yields are lower for reactions with pH 6 halide-ice films because lack of H^+ can effectively arrest reaction of HOBr after it binds to a halide ion on the ice surface. If no hydrogen ions are available in the vicinity of a bound HOBr adduct, then the reaction cannot continue forward. The HOBr adduct is stable and can remain attached to the halide-ice surface without reacting, or HOBr can desorb from the ice surface. It is for this reason that no connection between halide concentrations and product yields was observed. While halide concentrations determined the uptake of HOBr onto the halide-ice surface, gas-phase product formation was controlled by the availability of hydrogen ions in the neighborhood of the HOBr adduct.

Given the stoichiometry of (R9) and (R10), reaction of one HOBr molecule should have produced one Br_2 or one BrCl, depending on the particular reaction. However, product yields were significantly lower than 100%, suggesting formation of stable adducts on the surface. Low product yields might arise from a lack of hydrogen ions in the vicinity of $HOBr{\cdot}X^-$ adducts, where X is Cl or Br. Another alternative is that HOBr could initially bind to the ice surface via the $H^{\delta+}$ end of the molecule attaching to a halide ion on the ice. Indeed, the complexes so formed, $BrOH{\cdot}X^-$, are calculated to be about 1.5 kcal/mol more stable than their $HOBr{\cdot}X^-$ counterparts.[38] Adsorption to the surface in the configuration of $BrOH{\cdot}X^-$ would sterically inhibit BrX production.

Despite a wide variation in halide and hydrogen ion concentrations of the reactive surfaces, we observed an upper limit of about 0.01 to the uptake coefficient. This result is very different from values of 0.12 and 0.25, respectively, reported by Abbatt for the reaction of gas-phase HBr or HCl with HOBr on ice at

228 K;[20] the major difference in the reaction being the distribution and form of reactive components on the ice surface. One explanation for this difference may arise from the probability that HOBr will bind to the surface in the form of an adduct. This probability could be significantly less than unity if, for example, the bromide ions at the surface are strongly hydrated, if the HOBr collides in an unfavorable geometry for complex formation, or if the anionic surface sites are already occupied by an HOBr molecule; i.e., the surface is saturated. We also note that in contrast to the reaction between HOBr and HBr, where both reactants are delivered from the gas phase, it is quite likely that the bromide and hydrogen ions are physically separated in the film to some degree. In particular, when the temperature is taken below the eutectic temperatures of NaCl and NaBr, distinct domains consisting of ice and NaX (and concentrated H_2SO_4 solutions, in the case of the pH 2 solutions) may form. If hydrogen ions are separated from the NaX domains, then reaction may be somewhat disfavored. Although this would most likely affect the reaction probability for product formation, it may also have an effect on the overall uptake coefficient if the reaction occurs to some degree in a concerted manner.

Finally, we note that the mixed bromide/chloride film studied at 233 K behaved in a manner similar to the chloride-only films, with only BrCl observed as a product. This is likely due to the fact that the large excess of chloride ions in the film precludes the significant presence of bromide ions available at the surface, even though the amount of bromide in the film would have been enough to drive a reaction in a bromide-only film. We have previously observed the same behavior in the reaction of gaseous Cl_2 with bromide and mixed chloride/bromide films.[27] It is possible that had we been able to operate at significantly lower HOBr concentrations, a Br_2 product could have been observed before the (small) surface amounts of Br^- had been depleted.[26]

Experiments at 248 K. Given that 248 K is above the eutectic of the $NaBr-H_2O$ binary system (245 K),[39] the bromide-only films consisted of ice and a small amount of concentrated sodium bromide solution. In Figure 1b, we believe the HOBr signal returns to its starting value after HOBr exposure because the bromide ions in the surface solution have been consumed. As observed with aqueous solutions,[25] a significant acidity effect is evident with the reaction proceeding faster on more acidic films, and the product yields are somewhat higher than in the corresponding experiment at 233 K.

The most striking observation at 248 K is that both the chloride and the mixed films behaved as though there were considerably more chloride ions available for reaction, as would be the case if a solution were present. For this reason the HOBr signal does not recover after each exposure, and BrCl formation persists. Given that the eutectic temperature for the $NaCl-H_2O$ binary system is 252 K,[39] we had anticipated that the single component chloride films would be solid and consist of only ice and $NaCl \cdot 2H_2O$ hydrate, and that the chloride/bromide mixed films would consist of ice, $NaCl \cdot 2H_2O$ hydrate, and a small amount of NaBr in solution. However, as described in the paragraph above, this small amount of NaBr solution would not lead to the observed behavior.

It is not clear why films containing chloride behaved as would a liquid at a temperature below the $NaCl-H_2O$ eutectic. One possibility is that HOBr concentrations in the flow tube were high enough that HOBr interacted with concentrated chloride films in such a way as to cause them to melt. A similar phenomenon has been observed in the interactions of HCl vapor with water-ice films at roughly 200 K.[36] Confirmation of this hypothesis would require detailed phase transition studies of the $HOBr-NaCl-H_2O$ ternary system, which have not been performed to date.

The composition of the mixed films had an important effect on their reactivity. That HOBr reacted with only chloride ions in films containing 23% chloride/0.08% bromide at 233 K but reacted with both chloride and bromide ions at 248 K is most likely related to the different phases present at the two temperatures. Since 233 K is below the eutectic temperatures of both $NaCl-H_2O$ and $NaBr-H_2O$, mixed films at this temperature presumably consisted of ice, $NaCl \cdot 2H_2O$, and a small amount of $NaBr \cdot 2H_2O$.[39] Bromide ions were probably excluded from the surfaces of these films by the presence of approximately 288 times more chloride, rendering bromide inaccessible for reaction. In contrast, both ions were available for reaction in mixed films at 248 K because bromide ions were able to diffuse through the liquid to the reacting HOBr molecules.

Our results support predictions that both BrCl and Br_2 are products of (R9) and (R10) on sea salt aerosols in the marine boundary layer.[15] As the injector was pulled back in the experiment represented by Figure 3b, the HOBr signal dropped as HOBr adsorbed onto the halide film. HOBr reacted with chloride and produced BrCl, which gradually degassed from the film, as shown by the steplike increases in BrCl signal in Figure 3b. Br_2 was also produced, either by direct reaction of HOBr with bromide as shown in (R9), or by reaction of BrCl with bromide as described by (R11). On the basis of measured product yields of Br_2 and BrCl, the majority of Br_2 was formed from the direct reaction of HOBr with bromide ions. BrCl product yields were approximately the same for reactions with 23% chloride single component films as they were for reactions with 23% chloride/0.08% bromide mixed films at 248 K. If Br_2 had been produced via reaction of BrCl with bromide, then BrCl yields for the mixed system should have been less than those for reactions with chloride-only surfaces.

Summary and Atmospheric Implications

Below the eutectic temperature of $NaBr-H_2O$ our simulated sea ice surfaces have only chloride ions available for reaction with gas-phase HOBr. At temperatures above the $NaBr-H_2O$ eutectic point, both bromide and chloride ions are accessible in a reactive surface that contains liquid. Our data at 233 K are consistent with a mechanism where complex formation between HOBr and halide ions in the films occurs initially, followed by reaction with protons to give gas-phase products. For this reason, a pronounced acidity effect is seen in the product yields and product reaction probabilities. HOBr uptake coefficients are limited to a maximum of about 0.01, despite large variations in reactant ion concentrations. This is in contrast to reaction probabilities that approach unity in analogous heterogeneous reactions using gaseous reactants. It is important to note that in experiments of this type (and for ice samples from the field), the specific chemical nature of these surfaces is still not well characterized and may be affected by experimental conditions. In particular, with the HOBr concentrations used ($\sim 10^{12}$ molecules/cm^3) small surface concentrations of bromide may have been readily depleted and the 248 K films containing chloride may have melted to some degree.

For both (R9) and (R10), the reactions were slower than expected with initial uptake coefficients less than or equal to 0.01. These data are surprising because it has been previously assumed that the kinetics of HOX reactions on ice would scale with known rate constants for these reactions in the aqueous phase.[17,18] Chemistry of HOBr in acidic solutions is rapid: the third-order rate constant for (R9) at 298 K and 0.5 M ionic strength is $(1.6 \pm 0.2) \times 10^{10}$ M^{-2} s^{-1}.[29] For (R10), the third-order rate constant for the forward reaction has not been measured directly, but an upper limit of 5.6×10^9 M^{-2} s^{-1} can be calculated from the rate constant of the reverse reaction and the equilibrium constant for reaction R10, both of which have been experimentally determined.[28] This value is comparable to the rate constant for (R9). On the basis of these aqueous kinetic parameters, one can assume that the probabilities of (R9) and (R10) on ice would be relatively large and similar to each other, but our results in Tables 1 and 2 suggest that this may not be true. As an example, consider the HOCl reacting with bromide and hydrogen ion:

$$HOCl + Br^- + H^+ \rightarrow BrCl + H_2O \qquad (R14)$$

The heterogeneous ice chemistry of (R14), which is analogous to (R9), has been investigated previously using the same approach.[27] For reaction of gaseous HOCl with a pH 2, 0.1% bromide-ice film at 233 K, $\gamma = 0.051$. The measured third-order rate constant for (R14) in acid solution is 1.3×10^6 M^{-2} s^{-1};[40] this value is over 10 000 times smaller than the aqueous-phase rate constant for (R9). If the ice chemistry of HOX compounds were to scale with their aqueous-phase chemistry, the probability of (R9) should be unity. However, Table 1 indicates that $\gamma = 0.0082 \pm 0.0011$ for reaction of HOBr with a pH 2, 0.08% bromide-ice film at 233 K, which is over 5 times smaller than the corresponding HOCl value measured under almost identical experimental conditions. In fact, observed HOBr uptake coefficients were consistently smaller than the HOCl value of $\gamma = 0.051$. Our results suggest that it is not necessarily valid to infer kinetics for the interaction of HOBr with halide/ice surfaces from aqueous-phase rate constants.

Previous studies of HOBr heterogeneous reactions with other halogenated gases have been performed on ice,[20,21] in sulfuric acid solutions,[23] or on NaCl aerosols,[24] in contrast to looking at the direct reaction of HOBr with halide ions on ice surfaces. Only Kirchner et al. and Adams et al. have conducted similar experiments, although Kirchner et al. formed their films by spraying a halide solution onto the cooled inner walls of a flow tube, whereas Adams et al. used the method we employed.[19,26] Kirchner et al. operated with HOBr concentrations about 10 times higher than ours and Adams et al. operated with concentrations about 100 times lower. For reactions close to 233 K, at which all three groups have reported results on pH neutral chloride films, our HOBr uptake coefficient (1.8×10^{-3}, 23 wt % Cl^-) is in reasonable agreement with that of Kirchner et al. (1.24×10^{-3}, 18 wt % Cl^-, 230−240 K) but somewhat lower than that of Adams et al. (4.3×10^{-2}, 6.7 wt % Cl^-, 233 K). Adams et al. do not report values at 233 K for pure bromide films, but our result (8×10^{-3}, 5 wt % Br^-) is somewhat larger than that of Kirchner et al. (3.27×10^{-3}, 23 wt % Br^-, 230−240 K). For mixed films, our HOBr uptake coefficients (1.0×10^{-3}, 23 wt % Cl^- and 0.08 wt % Br^-, 233 K) are again in quite good agreement with the results of Kirchner et al. (1.42×10^{-3}, 18 wt % Cl^- and 0.06 wt % Br^-, 230−240 K) but are lower than those of Adams et al. (3.2×10^{-2}, 6.7% Cl^- and 0.024% Br^-, 233 K). For the mixed films at 233 K, Adams et al. report only Br_2 formation, Kirchner et al. report both Br_2 and BrCl formation, and we report only BrCl formation. It is important to highlight an additional result from Adams et al. indicates that their HOBr uptake coefficients decreased and their BrCl yields increased at higher HOBr concentrations. It is quite possible that our uptake coefficients and those of Kirchner et al. were lower than those of Adams et al. because our surfaces were being depleted of the reactive halides at the higher gas-phase reactant concentrations employed. Similarly, Br_2 and BrCl yields could also be affected by rapid depletion of small levels of surface bromide. Finally, in contrast to our results, Adams et al. did not observe a dependence of their kinetics on the film acidity; however, they only acidified their films to pH 4, whereas we took ours to pH 2. In our earlier study of the heterogeneous kinetics of HOCl on similar films, we saw that the kinetics were independent of acidity from pH 4 to 10 but that pH 2 films reacted significantly faster.[27]

To illustrate the amount of active halogen that may be released into the Arctic from this chemistry, we can model the reaction rate for HOBr loss on a sea ice surface using a dry deposition flux, *F*, as described previously:[27]

$$F = vC \qquad (E1)$$

In E1, v is the vertical deposition velocity of HOBr and C is its gas-phase concentration. The vertical deposition velocity of HOBr in the boundary layer is calculated from a resistance-in-series model that incorporates HOBr aerodynamic transport through the atmospheric surface layer, molecular diffusion to the sea ice surface, and loss by heterogeneous reaction.[41] The rate-limiting factor in the calculation of v is aerodynamic transport of HOBr, which depends on the relative turbulence and height of the atmospheric surface layer, local wind speed, and ice surface roughness. Hence, variations in reaction probability values of 1−2 orders of magnitude, i.e., of the size justified by the literature comparison just performed, will not significantly impact the total deposition velocity of HOBr.

Consequently, the dry deposition flux is effectively set by HOBr concentrations in the Arctic boundary layer and by meteorological factors. On the basis of field measurements, we take 10 ppt = 3.15×10^8 molecules cm^{-3} at 233 K as a steady-state concentration of HOBr in the springtime Arctic.[6] Using uptake coefficient values and BrCl product yields from Table 1 for reaction of HOBr with films containing 0.08% bromide and 23% chloride, and the calculated flux of HOBr lost via reaction on pH 6 and pH 2 ice surfaces at 233 K, we estimate that 1.1×10^7 molecules of gas-phase BrCl cm^{-3} (pH 6) and 1.6×10^7 molecules of gas-phase BrCl cm^{-3} (pH 2) are released over a period of 10 h into an air mass with a mixing height of 400 m. These concentrations, which correspond to BrCl mixing ratios of approximately 0.35 ppt (pH 6) and 0.51 ppt (pH 2) at 233 K, are comparable to other estimates of active halogen sources in the Arctic; e.g., see ref 22.

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