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Temperature dependent halogen activation by N_2O_5 reactions on halide-doped ice surfaces

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Abstract. We examined the reaction of N_2O_5 on frozen halide salt solutions as a function of temperature and composition using a coated wall flow tube technique coupled to a chemical ionization mass spectrometer (CIMS). The molar yield of photo-labile halogen compounds was near unity for almost all conditions studied, with the observed reaction products being nitryl chloride ($ClNO_2$) and/or molecular bromine (Br_2). The relative yield of $ClNO_2$ and Br_2 depended on the ratio of bromide to chloride ions in the solutions used to form the ice. At a bromide to chloride ion molar ratio greater than 1/30 in the starting solution, Br_2 was the dominant product otherwise $ClNO_2$ was primarily produced on these near pH-neutral brines. We demonstrate that the competition between chlorine and bromine activation is a function of the ice/brine temperature presumably due to the preferential precipitation of NaCl hydrates from the brine below 250 K. Our results provide new experimental confirmation that the chemical environment of the brine layer changes with temperature and that these changes can directly affect multiphase chemistry. These findings have implications for modeling air-snow-ice interactions in polar regions and likely in polluted mid-latitude regions during winter as well.

1 Introduction

The activation and recycling of inert halides from ice and snow surfaces into halogen atom precursors can have profound effects on atmospheric chemistry and composition (Finlayson-Pitts, 2010). For example, observations and modeling studies indicate that ozone and mercury depletion events, as well as enhanced oxidation of volatile organic compounds (VOC) that occur in lower tropospheric polar air are driven by vigorous catalytic halogen chemistry (Barrie and Platt, 1997; Bottenheim et al., 1990; Evans et al., 2003; Foster et al., 2001; Jobson et al., 1994; McConnell et al., 1992; Oltmans et al., 1989; Simpson et al., 2007b; Spicer et al., 2002). The chemistry is thought to be initiated and sustained by heterogeneous reactions occurring on sea ice, within salty snowpacks or on airborne halide-containing aerosol particles or blowing snow (Piot and von Glasow, 2008; Simpson et al., 2005; Simpson et al., 2007a; Yang et al., 2008; Yang et al., 2010; Zhao et al., 2008). Active halogen chemistry in the Arctic appears persistent in some regions while episodic in others, and it has been associated with air temperatures below 255 K, blowing snow, and time spent over first-year sea ice (Jones et al., 2009; Kalnajs and Avallone, 2006; Simpson et al., 2007a; Tarasick and Bottenheim, 2002). In addition, chlorine activation also occurs in other snow-impacted areas such as the polluted northern mid-latitudes during winter (Mielke et al., 2011; Thornton et al., 2010). The extent to which the snowpack in these regions affects halogen cycling remains uncertain.

While active halogen chemistry in the Arctic has become well characterized by observations, the multiphase chemistry required to explain the observations remains relatively uncertain. For example, based on hydrocarbon reactivity measurements, the ratio of bromine to chlorine atoms has been inferred to range from 80–990, and exhibit significant variability (Boudries and Bottenheim, 2000; Cavender et al., 2008; Keil and Shepson, 2006). Standard chemical mechanisms employed under Arctic conditions generally find Br/Cl of 1000 or greater (Keil and Shepson, 2006; Michalowski et

al., 2000); thus the observations imply a missing net chlorine atom source relative to bromine that is a factor of 10, or more, larger than currently in such models. Partly responsible for such problems is our limited understanding of the air – ice interface under typical environmental conditions. It is likely that on sea ice, snowpacks, and airborne snow particles there is a rich liquid brine layer, containing relatively high concentrations of halide and other inorganic ions, as well as organic compounds, which have been excluded from the water-ice matrix (Grannas et al., 2007; Koop et al., 2000). Moreover, the physical and chemical properties of this brine layer depend upon meteorological conditions such as temperature and relative humidity, as well as upon chemical processing and exposure to depositional sources of salts and acids (Cho et al., 2002; Koop et al., 2000; Morin et al., 2008; Sander and Morin, 2010). Experiments that probe multi-phase chemistry as a function of these parameters are generally lacking and as such the efficiency of several key reactions under typical environmental conditions remain unknown.

Here we present results of a study in which we exposed known concentrations of gaseous N_2O_5 to a range of halide-doped ice surfaces under varied conditions. The motivation for this specific system is two-fold. First, to our knowledge, the reactivity and products of N_2O_5 reactions on halide-doped ice systems under Arctic or wintertime mid-latitude conditions has not been explored. N_2O_5 chemistry presumably occurs, albeit at low levels, in the vicinity of Arctic halide-doped ice systems due to the presence of anthropogenic NO_x sources such as high latitude urban areas, commercial shipping, and oil and gas exploration, and due to the production of NO_x via nitrate photolysis in snowpacks (Honrath et al., 1999). Moreover, halide-doped snow also exists in continental mid-latitude regions during winter, and often where NO_x emissions are large, either due to sea salt and playa dust deposition or possibly from road salt or halide de-icing fluids applied to roadways. Whether the snowpack is a source of reactive halogens in these latter regions remains unknown. Second, the chemistry of halogen activation by reactions of N_2O_5 in aqueous solutions and on solid salts is reasonably well studied (Behnke et al., 1997; Bertram and Thornton, 2009; Roberts et al., 2009; Thornton and Abbatt, 2005). This knowledge therefore provides a means to probe our understanding of brine layer composition and its dependence on physical properties such as temperature. Such information will allow for better estimates of the rates and product yields of other multiphase reactions occurring in halide-doped ice systems.

2 Experimental

Experiments were conducted using a frozen wetted wall flow tube coupled to a custom-built chemical ionization mass spectrometer optimized for the detection of gas phase halogen species. A schematic diagram of the experimental set-up is shown in Fig. 1.

2.1 Temperature controlled flow tube reactor

The reaction of N_2O_5 on halide-doped ices is carried out in a 20 cm long, 2.5 cm OD wetted wall pyrex tube that is housed in a temperature controlled cooling jacket. The cooling jacket consists of a 24 cm long, 2.5 cm ID stainless tube welded in the center of a $25 \times 25 \times 15$ cm^3 stainless steel bath containing ~5 l of 95 % ethanol. The bath is first cooled to 240–250 K using a commercial chiller (Thermo), and then further by the addition of dry ice to create a dry ice/ethanol slurry. The liquid level of the bath was maintained at a height of 5 cm above the cooling jacket. Precise temperatures in the flow tube region are obtained by adding either room-temperature ethanol (for warmer conditions) or additional dry ice (for colder conditions) until the desired temperature is reached.

2.2 Ice surfaces

The reaction of N_2O_5 was carried out on artificial sea ice surfaces. Artificial halide ion solutions were made using 18MΩ water and NaCl and NaBr from Aldrich without further purification. A stock synthetic seawater solution was made from 35.00 g SeaChem Marine Salt (see Table 1) dissolved in 1 l DI water, giving a relative chloride to bromide mole ratio of 650:1. While containing typical seawater carbonate buffering capacity, the pH of these solutions was initially 8.4 but due to uptake of acids from room air during preparation and from the N_2O_5 reaction, the brines were likely slightly acidified. No detectable change in products was observed upon several repeated N_2O_5 exposures to a given ice tube suggesting that any changes in pH were not important to the overall product distribution. A conclusive measurement of the pH of the thin films was not possible. Additional synthetic solutions were prepared by adding various amounts of NaBr to 100 ml samples of the stock solution to create new solutions with Cl:Br ratios lower than that of seawater. In this way, total ionic strength was not conserved, but uniformly increased as the Cl:Br ratio was decreased due to the addition of NaBr. The perturbation to total ionic strength is therefore small for most of the Cl:Br ratios probed here, ranging from 650:1 to 1:1, but typically at or higher than 30:1. In general throughout this manuscript, Cl:Br ratios are mole ratios.

Ice coated flow tubes were prepared by first etching the inner pyrex walls with 2 % HF, which produces a contaminant-free wettable surface (Abbatt and Molina, 1992; Abbatt, 1994). The glass tube was then rinsed copiously with DI water and baked. The tube was then coated thoroughly with a halide solution and manually rotated to ensure a uniform liquid coating. The flow tube was then placed into the cooling jacket and rolled so that ice formation was uniform over the entire surface. A carrier flow of 1250 standard cubic
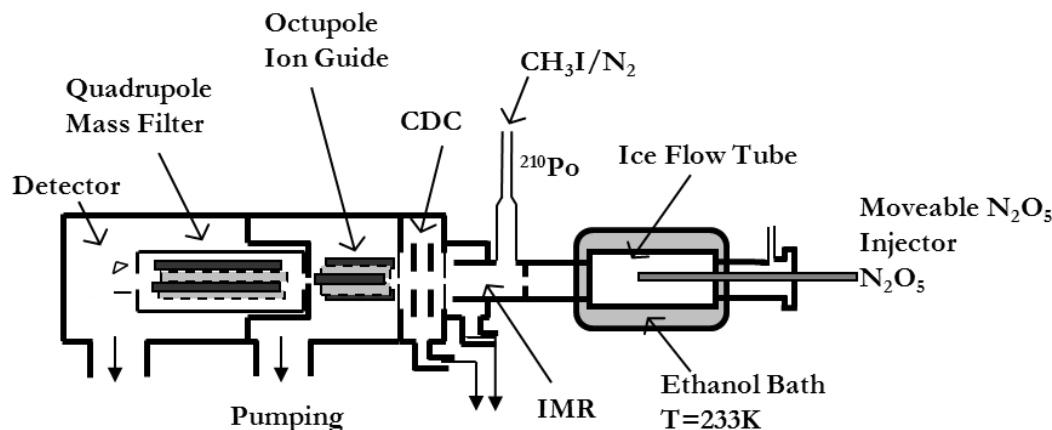
Fig. 1. Schematic of the ice-coated wall reactor and CIMS apparatus.

centimeters per minute (sccm) of dry N_2 was passed through two copper cooling coils, and then added at the entrance of the flow tube. The bulk flow led to a residence time of 0.14 s per cm of ice exposed to reactants, with a maximum interaction time of 3 s possible for a fully exposed ice tube. The temperature of the ice surface was measured throughout the course of an experiment using a fine gauge type-K thermocouple in contact with the ice surface. The temperature of the ice surface and the N_2 flow at the exit were usually within 5 K, which we take as our ice temperature measurement accuracy. The ice coated flow tubes were allowed to equilibrate under a conditioned N_2 flow for 10–15 min prior to exposing them to N_2O_5.

2.3 N_2O_5 synthesis and delivery

N_2O_5 is synthesized using one of two similar methods described here briefly. The first method involves a 20 cm long, 3 cm OD glass reaction cell, where the reaction of a small amount of NO_2 with excess O_3 occurs at ambient temperatures producing N_2O_5 gas. O_3 is generated by flowing ∼500 standard cubic centimeters per minute (sccm) of O_2 by a pen ray (UVP) lamp. Pure N_2O_5 is trapped in a glass cold finger held in an ethanol/liquid-N_2 slurry and subsequently stored at 220 K. During experiments, the N_2O_5 sample is kept in the temperature range of 200 to 205 K in a slurry of ethanol and dry ice. The N_2O_5 is swept out of the cold trap by passing 10 sccm of dry N_2 through the trap; this flow is then diluted by 90 sccm of dry N_2 for transit from the trap to the flow reactor. Most experiments were conducted using the second synthesis method which involves a similar system; however, it does not involve N_2O_5 pre-collection or storage, and is made on demand by a custom-built gas-synthesis apparatus described previously (Bertram et al., 2009; Kercher et al., 2009). In this method 3 sccm of medical-grade zero air is mixed with 40 sccm of pure N_2 and passed by a pinhole, behind which is a UV lamp, to produce a relatively low con-

centration of ozone (few ppm). Ozone is subsequently mixed with NO_2 in a 2.5 cm ID Teflon tube producing N_2O_5. The second method provides more stable output as small temperature fluctuations in the solid N_2O_5 trap of the first method can lead to large and rapid variations in N_2O_5 delivered to the flow reactor. As in the first method, a small flow of dry N_2 (100 sccm) delivered the N_2O_5 and any remaining NO_2 and O_3 to the injector.

The injector is 3 mm OD PFA tube surrounded by a 6 mm OD glass tube to provide support. The injector is positioned in the center of the wetted wall flow tube. Once the effluent of the injector mixed with the carrier flow, the resulting mixing ratio of N_2O_5 prior to exposure to the ice surfaces was 2–4 ppb ($5–10 \times 10^{10}$ molec cm^{-3}). The concentrations of NO_2 and O_3 were both approximately 50 ppb (Bertram et al., 2009; Kercher et al., 2009). In order to test the effects of NO_2 and O_3 being present, a set of ice tubes were exposed to NO_2 and O_3 separately. No halogens were detected during these tests suggesting that only the N_2O_5 exposure produced halogens under our conditions. While an ice tube was equilibrating, the injector opening was located passed the downstream exit of the coated wall flow tube so as to not expose the ice to N_2O_5. Then, during the course of an experiment, the injector was repeatedly pulled back to expose the ice surface to N_2O_5 for approximately 2-min intervals, during which the gas phase products and loss of N_2O_5 were monitored by the mass spectrometer.

2.4 Detection of gas phase reactant and products

N_2O_5, $ClNO_2$, Cl_2, BrCl, $BrNO_2$, and Br_2 were all monitored online by a CIMS using iodide clusters. We have described our development of this ion chemistry in detail previously (Kercher et al., 2009; McNeill et al., 2006), and it has since been applied to the detection of Cl_2, Br_2 and BrO either in laboratory or field settings (Liao et al., 2011; Mielke et al., 2011; Neuman et al., 2010; Roberts et al., 2009). To

our knowledge, detection of BrCl and $BrNO_2$ by this method has not been described, but is a readily straightforward extension. In all cases, we report signals measured at the cluster ions, $I(M_i)^-$, corresponding to each isotope of the parent mass of each halogen-containing molecule (M_i). Iodide ion chemistry also produces other less specific reaction products from halogens and N_2O_5 that we monitored as well for further confirmation of product identities (Kercher et al., 2009).

A field deployable CIMS, that has been robustly calibrated to N_2O_5, $ClNO_2$, and Cl_2 as part of several campaigns was used for these experiments (Kercher et al., 2009; Thornton et al., 2010). As part of the field experiments we have established absolute sensitivities and more importantly a robust estimate of the sensitivity to N_2O_5 relative to that for $ClNO_2$ by using standard additions of N_2O_5, quantified with an internally calibrated cavity ringdown spectrometer, and the conversion of this N_2O_5 on wetted NaCl salt beds. Furthermore, we have tied the $ClNO_2$ sensitivity to that of Cl_2 by employing a Cl_2 permeation tube (KIN-TEK) during the field campaigns and these laboratory measurements. The output of the permeation tube was certified by the manufacturer and confirmed by gravimetric analysis. A Br_2 permeation tube (KIN-TEK) was also used during the experiments described here to calibrate the associated Br_2 signals. BrCl standards were generated by mixing the output of the Br_2 and Cl_2 permeation tube with the Cl_2 and Br_2 in a shrouded long residence mixing chamber prior to delivery to the CIMS. Finally, the calibration to $ClNO_2$ and $BrNO_2$ was periodically checked by passing Cl_2 or Br_2, respectively, over a dry $NaNO_2$ salt bed (Mielke et al., 2011). We have separately assessed the conversion efficiency of Cl_2 to $ClNO_2$ on $NaNO_2$ beds during the field experiments by comparing to the $ClNO_2$ produced by calibrated N_2O_5 conversion on NaCl beds. Through repeated calibrations both during field campaigns and in these experiments, we estimate an uncertainty in the benchmark N_2O_5 and $ClNO_2$ sensitivities to be $\sim$25 % (Kercher et al., 2009; Thornton et al., 2010). Therefore, we are able to report absolute yields that have an accuracy of $\pm$25 %. A single set of average sensitivity values are applied to all experiments, neglecting variations in on the hourly or even daily timescales. The total halogen yield varies between about 0.8 and 1.2 on average across all the relevant experiments, similar to the expected variability based on the uncertainty discussed above. The absolute yield variations likely represent changes in the sensitivity to N_2O_5 relative to that for the halogen species likely due in large part to applying a constant calibration to all data. Changes in the relative product yields due to changes in ice composition, on which our conclusions are mostly based, are likely more accurate as the only requirement is that the instrument sensitivity is constant as the ice composition is varied over the timescale of a few hours.

When sampling air with a relative humidity greater than $\sim$40 %, we have found that the instrument has a similar sensitivity, 1–3 counts/pptv/sec, to all of the above species when

Table 1. Concentration of components in synthetic seawater made from "Marine Salt" purchased from manufacturer (Seachem) and diluted into MilliQ water as per manufacturer recommendations. The synthetic seawater formed the basis for frozen halide solutions.

Component	Concentration ($mg\,l^{-1}$)
Chloride	19 336
Sodium	10 752
Sulfate	2657
Magnesium	1317
Potassium	421
Calcium	380
Carbonate/Bicarbonate	142
Strontium	9.5
Boron	16
Bromide	56
Iodide	0.06
Lithium	0.3
Silicon	< 0.1
Iron	0.0098
Copper	0.0003
Nickel	< 0.015
Zinc	0.0107
Manganese	0.0023
Molybdenum	0.0098
Cobalt	0.0004
Vanadium	< 0.015
Selenium	< 0.019
Rubidium	0.118
Barium	< 0.04

monitored as the Iodide clusters. As this experiment aimed to vary the temperature of an ice-coated flow tube, the water vapor content of the flow sampled by the CIMS would potentially be low and variable. Thus, to maintain a constant calibration across the conditions probed, a flow of humidified N_2 was added after the flow exited the ice tubes but prior to detection. This additional flow established and maintained the relative humidity sampled by the CIMS at 45 ± 2 %.

3 Results and discussion

The reaction of N_2O_5 on synthetic sea ice was investigated as a function of temperature and the relative Cl:Br concentration. A typical time trace showing results for the reaction of N_2O_5 on a natural sea ice surface at 242 K is shown in Fig. 2. The various ion signals are plotted as a function of the experiment time. The black trace shows the N_2O_5 signal, high when it is bypassing the ice surface. Upon exposing the ice surface to N_2O_5, halogenated species including $ClNO_2$ (blue), and Br_2 (red) are promptly produced with a total halogen yield per N_2O_5 reacted near unity. In general, $ClNO_2$ and Br_2 were the only halogens detected – Cl_2, BrCl, and $BrNO_2$ were never reproducibly detected, and the absolute
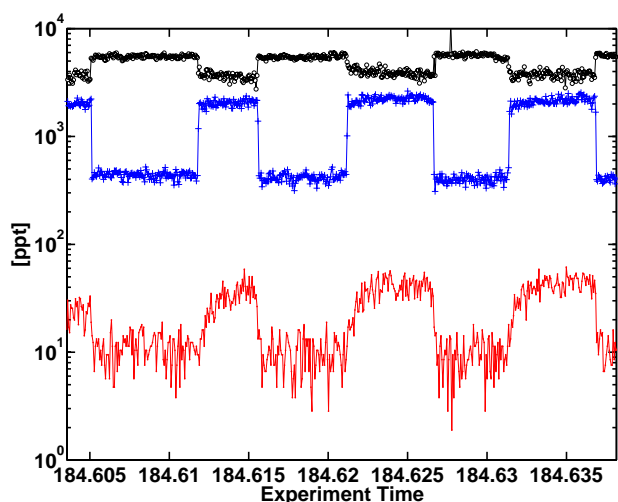
Fig. 2. An example experimental time series showing calibrated ion signals in mixing ratio units (pptv) during which a halide-doped ice surface was repeatedly exposed to N_2O_5. N_2O_5 signal (black circles), is high when it is bypassing the ice surface, and lower during exposure. Upon exposing the ice surface to N_2O_5, halogenated species including $ClNO_2$ (blue crosses), and Br_2 (red line) are promptly produced with a total halogen yield per N_2O_5 reacted near unity.
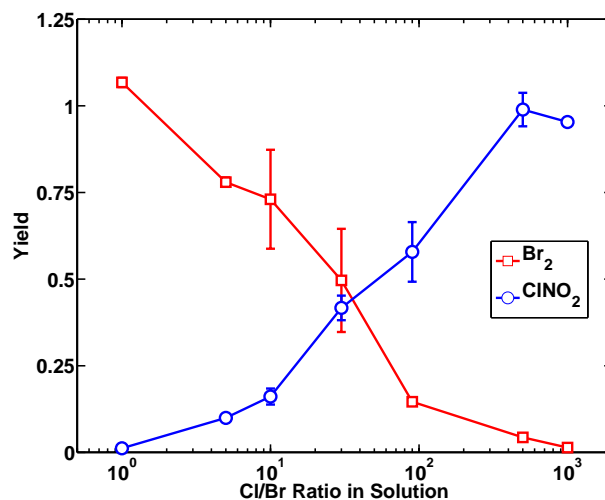

Fig. 3. The dependence of halogen products on the relative concentration of chloride and bromide in the aqueous solution used to form the ice-coated flow tube. The error bars represent the 1σ deviation of multiple determinations at each Cl:Br. The temperature of the ice surface was 258 K, therefore precipitation effects are not expected. Equal activation of $ClNO_2$ and Br_2 occurs at approximately 30:1 Cl:Br. The reaction of N2O5 with liquid water is inferred to be unimportant, consistent with the low mole fraction of H_2O relative to the halides expected in the brine.

yields of $ClNO_2$ and Br_2, determined from the calibrated signal changes, were essentially always large enough to account for all N_2O_5 reacted within experimental error. The halogen yields obtained under various conditions and discussed below are determined from time traces such as this one.

The apparatus used here was aimed at product determination and not reaction kinetics. Given the large diameter of the ice tube and the operation of the flow reactor at atmospheric pressure, we expect the rate of N_2O_5 reaction on the ice coated walls to be limited by gas-phase radial diffusion from the tube center to the walls. As a check on this expectation, a set of experiments was conducted during which the loss of N_2O_5 and production of halogens on a sea ice surface were monitored during incremental pullbacks of the injector, exposing more ice surface with each pullback (not shown). The natural log of N_2O_5 signal, averaged for a total of 6 decays on three separate ice tubes, as a function of injector position yielded an observed first order rate coefficient of $0.27 \pm 0.04 \, \mathrm{s}^{-1}$, which is consistent with the $0.29 \, \mathrm{s}^{-1}$ expected for diffusion-limited transfer from the tube center to the wall (Pöschl et al., 1998). For a reaction probability per N_2O_5 collision with the ice coated wall, $\gamma(N_2O_5)$, that is $>10^{-4}$, reaction at the wall becomes faster than diffusion to the wall. As our data indicates diffusion limited loss, we can therefore only report 10^{-4} as lower limit to the $\gamma(N_2O_5)$ on synthetic sea ice. Hanson and Ravishankara (1991) measured $\gamma(N_2O_5)$ on pure water ice to be 0.02, consistent with our lower limit.

3.1 Product dependence on the Cl:Br mole ratio

There have been relatively few studies of the direct competition between chloride and bromide ions for reaction with N_2O_5 in aqueous solutions (Behnke et al., 1997), and none to our knowledge in ice systems. We therefore varied the mole ratio of chloride to bromide ions (Cl:Br) in the solutions used to create the ice surfaces and measured the various halogen products that were released upon exposure to N_2O_5. In Fig. 3 the absolute yields of the dominant gas phase products, $ClNO_2$ and Br_2 are shown as a function of the Cl:Br in the solution that was frozen and held at 258 K. Each point represents the average of several determinations at each Cl:Br ratio, the error bar represents the 1σ deviation of points averaged. The total halogen yield per N_2O_5 reacted remained near unity at each Cl:Br ratio tested and the only halogenated products observed were $ClNO_2$ and Br_2. At high Cl:Br ratios, typical of seawater ($\sim$650:1 Cl:Br), $ClNO_2$ was the dominant product of N_2O_5 reactions on sea ice, comprising essentially 100 % of the total halogen yield. However, as the relative concentration of bromide increased, Br_2 production increased at the expense of $ClNO_2$. At a Cl:Br ratio of 30:1, Br_2 and $ClNO_2$ were produced at nearly equal yield. Once the Cl:Br ratio reached 1:1, $ClNO_2$ production was negligible and Br_2 comprised essentially 100 % of the total halogen yield.

While not the focus of this work, we can discuss a possible mechanism for N_2O_5 reactions in the brine layer of halide-
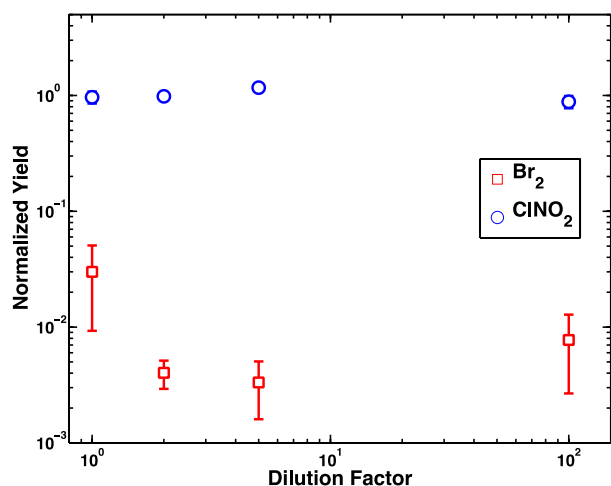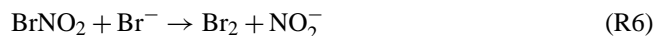
Fig. 4. The normalized yields of products of the reaction of N2O5 on synthetic sea ice surfaces are plotted as a function of the dilution factor applied to a standard seawater solution (Cl:Br = 650:1) prior to freezing. The absolute yields ($\Delta S_{halogen}/\Delta S_{N_2O_5}$) measured at dilution factors >1 are normalized to the average total halogen yield (~1) from multiple determinations on synthetic sea ice (dilution factor =1). A dilution factor of 1 corresponds to a salinity of 35 parts per thousand in the solution prior to freezing, while a dilution factor of 10 corresponds to 3.5 parts per thousand and so on. The results are consistent with the fact that as the ice freezes it rejects the salts into a highly saline interface layer – the ionic composition of which is set by humidity and temperature. The error bars represent the 1σ deviation of multiple determinations in each dilution factor bin.

doped ice systems. We assume the following reactions are occurring:

$$N_2O_5 \rightarrow NO_2^+ + NO_3^- \qquad (R1)$$

$$NO_2^+ + Cl^- \rightarrow ClNO_2 \qquad (R2)$$

$$NO_2^+ + Br^- \rightarrow BrNO_2 \qquad (R3)$$

$$NO_2^+ + H_2O \rightarrow HNO_3 + H^+ \qquad (R4)$$

$$ClNO_2 + Br^- \rightarrow BrNO_2 + Cl^- \qquad (R5)$$

$$BrNO_2 + Br^- \rightarrow Br_2 + NO_2^- \qquad (R6)$$

We have no evidence for the formation of the NO_2^+ intermediate. Its formation (R1f) and loss (R1r, R2, R3, or R4) may occur as one concerted reaction with nucleophilic attack of an electron-deficient nitrogen in the already solvated N_2O_5, which we designate as NO_2^+. Previous work in aqueous solutions suggests that $k_{(R3)} < 1000 k_{(R2)}$ (Behnke et al., 1997). BrNO2 was not detected from our ice tubes. However, we were able to produce and detect it via conversion of Br2 on a NaNO2 salt bed, albeit with less reproducibility as for ClNO2. Therefore, the rate of Reaction (R6) may be

faster than the desorption of BrNO2 from the brine layer under the conditions of our experiments. That said, we cannot neglect some conversion of BrNO2 to Br2 in the ~1 m length of Teflon tubing between the flow reactor exit and our CIMS. Importantly, previous work has demonstrated that BrNO2 reacts efficiently to Br2 on aqueous bromide solutions (Fickert et al., 1998; Frenzel et al., 1998; Schweitzer et al., 1998). For example, Fickert et al. (1998) showed that after 0.5 s of exposure of ClNO2 to 1×10^{-4} M bromide solutions, Br2 was 80 % of the products while BrNO2 was the remainder. Our interaction times (seconds) and bromide ion concentrations in the brines (>~0.005 M) are generally much larger than those of Fickert et al. especially at the lowest Cl:Br ratios employed, suggesting that some combination of increases in the rates of Reactions (R3) and (R5) also occur upon decreasing the Cl:Br ratio in the frozen solutions.

If we assume that N_2O_5 either reacts with chloride or bromide to first make the corresponding nitryl halide, then our results are consistent with $k_{(R3)} \sim 30 k_{(R2)}$ based on the Cl:Br ratio at which Br2 production equals that of ClNO2 and the assumption the Cl:Br ratio in the solution that is frozen is preserved in the resulting brine. That $k_{(R3)}$ might be larger than $k_{(R2)}$ is also consistent with the lower oxidation potential of bromide ions relative to chloride (Haynes and Lide, 2011). BrCl was never observed in our system, which is also consistent with the results of Fickert et al. (1998) who found no evidence for BrCl as a product of Reaction (R5) in aqueous solutions. To conclude this section, we note that there is a general correspondence between similar reactions studied in aqueous systems and the ice systems used here, which suggests that the ice brines are to first order behaving similarly to aqueous solutions, and that there are not large relative changes in the relevant reaction rate constants with temperature over the range of 258–298 K. In what follows, we use these observations of product yields and their dependence on the Cl:Br mole ratio as constraints to understanding how the Cl:Br ratios in the brines change with temperature.

The above experiments varied the mole ratio of chloride relative to bromide prior to freezing, while maintaining the total ion activity similar to that of sea water. We also tested the effect of diluting the initial synthetic seawater solution (650:1 Cl:Br) with pure DI water prior to freezing, and found no significant changes (<25 %) in the total halogen yield with dilution factors of up to 100. The results are shown in Fig. 4 and are consistent with the fact that as the ice freezes it rejects the salts into a highly saline interface layer. To better isolate the effect of dilution and reduce noise likely due to day-to-day calibration drifts, the absolute yields for a given dilution factor are normalized by the average total halogen yield determine on synthetic sea ice (dilution factor 1). Upon freezing and as the temperature is lowered further the liquid water concentration (mass fraction) in the remaining solution is greatly reduced such that the reaction of N_2O_5 on the brine interface layer primarily produces halogen products apparently even when freezing a very dilute salt solution. This
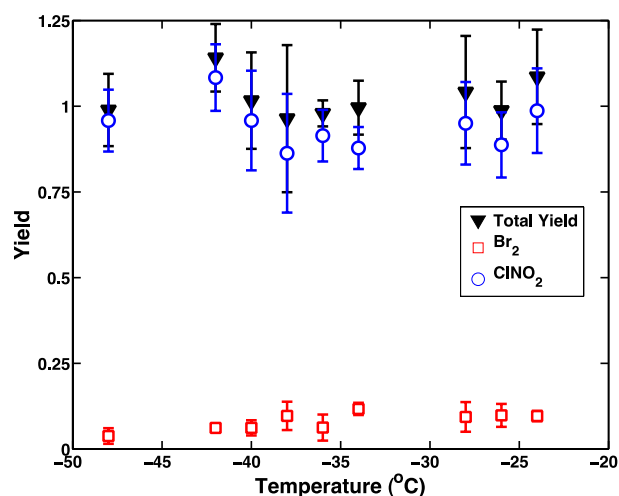
Fig. 5. Halogen product yields are plotted as a function of ice temperature. The error bars are one sigma standard deviations in the temperature bins. The same synthetic seawater solution (salinity of 35 parts per thousand and Cl:Br of 650:1) was used to make the ice in all cases. No significant changes in halogen products is observed across the temperature range studied, as is consistent with the competitive mechanism (shown in Fig. 3) because the Cl:Br mole ratio in the corresponding brines theoretically remains above ∼100:1.

result suggests that even ice or snow samples that are relatively dilute in halide content relative to total water equivalent of the snow may still drive the halogen yield from N_2O_5 reactions to unity if the brines remain accessible at the ice-air interface.

3.2 Product dependence on temperature

The ionic content of brine layers formed when seawater freezes is known to be a function of temperature. As temperature decreases past the freezing point of water in the halide salt solution, water ice precipitates enhancing the ionic content of the remaining brine (Lodge et al., 1956). As temperature decreases further various salt hydrates precipitate, in particular, NaCl2H$_2$O and MgCl$_2$12H$_2$O precipitate out of the brine at temperatures of 250 and 235 K respectively (Marion and Farren, 1999; Morin et al., 2008; Richardson, 1976; Sander et al., 2006; Sander and Morin, 2010). The precipitation of chloride salts changes the relative concentration of chloride to bromide in the brine layer. At a temperature of 230 K, freezing and precipitation processes result in an enhanced net concentration of bromide ions such that the Cl:Br ratio in frozen seawater decreases from 650:1 to 100:1 (Koop et al., 2000; Morin et al., 2008). However, there is limited evidence that multiphase chemistry which might occur in the ice brines is sensitive to such changes. Moreover, it is useful to have an independent verification that such temperature dependent composition changes occur generally and are not kinetically limited in some way as most experiments and

theory have assumed or sought thermodynamic equilibrium (Koop et al., 2000; Morin et al., 2008).

To examine the above issues, we use the Cl:Br dependent product yield from the N_2O_5 reaction on halide-doped ices held at 258 K (Fig. 3) as a guide for interpreting changes in the product yield as the ice temperature is decreased from 255 K to 220 K. Changes in the product yields are then interpreted as being due to temperature induced changes in the Cl:Br ratio of the corresponding brine. We performed two sets of experiments in this regard. In the first, we simply froze synthetic seawater solutions to different temperatures and exposed them to N_2O_5. In the second set of experiments, we further enhanced the bromide content of the seawater solution so that we started with Cl:Br mole ratios of 100:1, 50:1, and 30:1. These solutions were then each frozen at different temperatures and exposed to N_2O_5.

In Figure 5, we show the product yields per N_2O_5 lost on frozen synthetic sea water solutions (Cl:Br = 650:1) at various temperatures. ClNO$_2$ was the dominant product across the entire temperature range examined for this system and only trace bromine containing products were observed. The dominance of ClNO$_2$ can be attributed to the high concentration of chloride relative to bromide in the initial solution, on the order of 650:1. Moreover, even after NaCl2H$_2$O and MgCl$_2$12H$_2$O have precipitated from the brine at temperatures below 238 K, the Cl:Br mole ratio in the brine is still ∼100:1 for sea water (Koop et al., 2000; Morin et al., 2008). Based on the competitive mechanism illustrated in Fig. 3 above, ClNO$_2$ should remain the dominant product even at these conditions. Therefore, to increase the systems sensitivity to changing temperature, we examined the temperature dependence of brines having higher initial bromide content.

The results from a series of initial Cl:Br mole ratios of 100:1, 50:1 and 30:1, subjected to varying temperatures are shown in Fig. 6. For clarity, the data were averaged into equal-point temperature bins, and the vertical error bars are 1σ deviations about the average yields for each bin. The horizontal error bars represent the estimated accuracy of our ice temperature measurements (see methods). The standard deviation of temperatures probed in a given bin is on the order of the size of the data points. This bin averaging inevitably smears across some sharp transitions, and we more fully test all the data in a subsequent section (Fig. 7). Ice tubes from these solutions were placed into the flow tube reactor initially held at a temperature near 260 K, and then cooled to a given temperature. The ice was then exposed to N_2O_5 to determine the product yields, and the process was repeated for different temperatures with the same starting solution, and then this approach was repeated again for different starting solutions, usually on separate days. In each panel of Fig. 6, we show the yield of ClNO$_2$, Br$_2$, and the total halogen yield (sum of ClNO$_2$ and Br$_2$). Here we focus on the relative changes between ClNO$_2$ and Br$_2$ for a given ratio of Cl:Br. For an initial starting ratio of 100:1 Cl:Br (far right panel), ClNO$_2$ and Br$_2$ are both produced at the approximate ratio expected from the
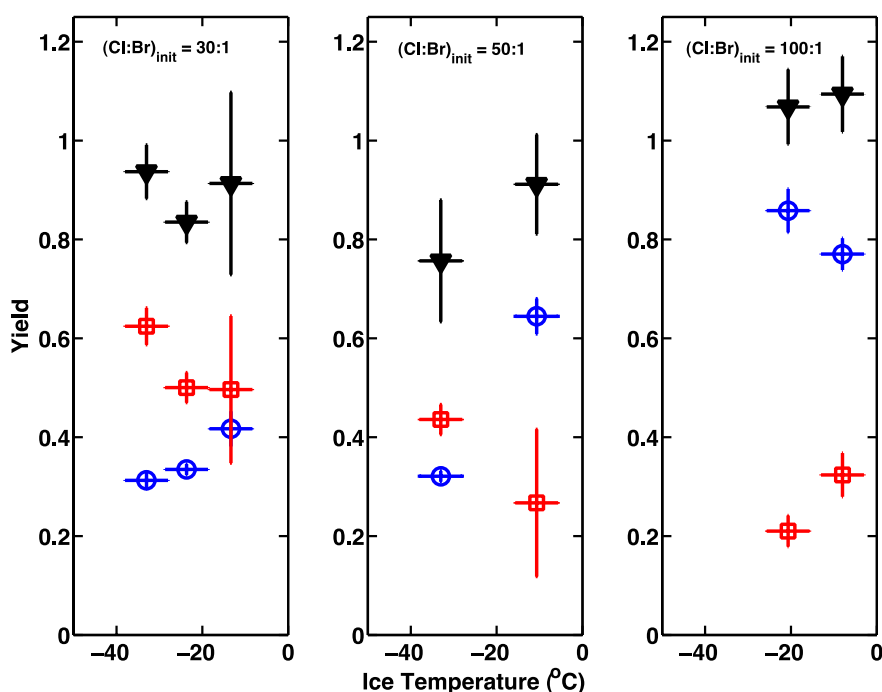
Fig. 6. Halogen product yields are plotted versus ice temperature for three different starting solutions. The vertical error bars represent the 1σ deviation of the yields from multiple determinations and the horizontal error bars are $\pm$ 5K (see methods) representing the estimated ice temperature accuracy. The initial solutions are synthetic seawater with additional bromide to enhance the starting Cl:Br mole ratio to be 100:1, 50:1, and 30:1. Cooling the ices formed from the various initial solutions below the temperatures at which precipitation of NaCl2H$_2$O and MgCl$_2$12H$_2$O occurs led to enhanced production of Br$_2$ beyond that expected from the initial Cl:Br ratio. This result is consistent with a decrease in the Cl:Br ratio of the brine layer due to precipitation of the chloride containing salts at temperatures below 250 K.
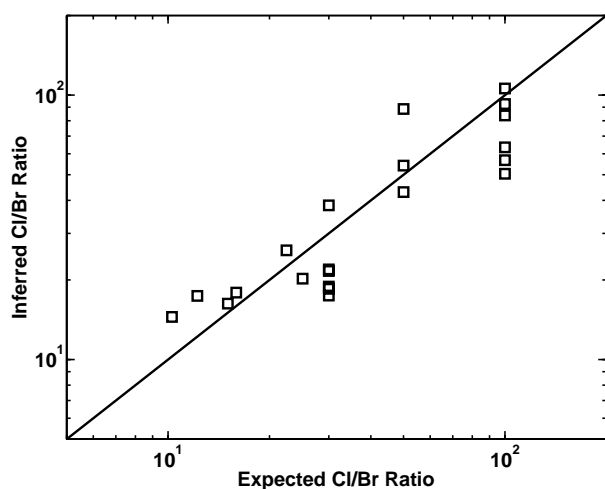

Fig. 7. The Cl:Br ratio in the brine interface layer inferred from our observations (Figs. 3 and 6) is plotted versus Cl:Br ratio predicted from a thermodynamic model of the temperature-dependent brine composition for the conditions tested in our experiment. See text for details. The two estimates are broadly explained by a 1:1 relationship (shown as solid line).

data in Fig. 3. Upon cooling to near the NaCl2H$_2$O precipitation temperature, there is no corresponding increase in Br$_2$ yields. Starting with a 50:1 Cl:Br solution (middle panel), ClNO$_2$ is again the dominant product above the NaCl2H$_2$O precipitation temperature, but upon cooling the ice tube walls to below 245 K, Br$_2$ is preferentially activated by the reaction N$_2$O$_5$. Similarly, using a 30:1 Cl:Br solution, the yields of ClNO$_2$ and Br$_2$ are nearly equal above the NaCl2H$_2$O precipitation temperature and Br$_2$ is again preferentially produced at colder temperatures and to a larger extent than for the 50:1 Cl:Br ices. These results are consistent both with the observations made by varying Cl:Br in ices at one temperature (258 K), shown in Fig. 3, and with the expected changes of the Cl:Br in ice brines due to precipitation of chloride containing salts at temperatures below 250 K (Morin et al., 2008).

We end this section with a discussion of the extent to which we obtained closure between observed and predicted changes in brine composition with temperature. We use the observed product yields determined at various temperatures (Fig. 6) and the yield dependence on the Cl:Br mole ratio determined from Fig. 3 to infer the Cl:Br ratio of the brines at different temperatures. We then compared these "inferred" Cl:Br ratios to those expected based on the initial Cl:Br of

the starting solutions and the bromide enrichment factor as a function of temperature from the thermodynamic model of Morin et al. (2008). The results are scattered in Fig. 7, and generally fall along a 1:1 line, suggesting that we reasonably understand and can predict the availability and competition of halide ions in the brine interface layer as a function of temperature and the bulk Cl:Br ratio of the initial solution. Nonetheless, the actual situation in environmental ice systems may be more complex due in part to brine movement through the snowpack and sea ice, and freeze-thaw cycles.

4 Conclusions

We have demonstrated that the reaction of N_2O_5 on halide-doped ice surfaces produces reactive halogen atom precursors at near unit yield across a broad range of compositions and temperatures. We find that for Cl:Br mole ratios in the resulting ice brine greater than about 30:1, $ClNO_2$ is the dominant product, while below this threshold Br_2 is the dominant product. Furthermore, the temperature dependence of the halogen product yields was found to be consistent with expectations that the brine composition, and in particular the Cl:Br mole ratio, is temperature dependent due to the preferential precipitation of chloride containing salts from the brine at temperatures less than 250 K. The Cl:Br mole ratio can vary downwind of sea salt sources and with depth in a snowpack (Simpson et al., 2007b), thus N_2O_5 has the potential to activate bromine or chlorine depending on the exact composition of the halide-doped ice. As acid deposition and alkalinity precipitation can lead to actual environmental brines that are acidic (Sander et al., 2006), N_2O_5 reactions on snowpacks or lofted ice particles may in fact be a Cl_2 source via conversion of $ClNO_2$ (Roberts et al., 2008).

Our findings have implications not only for the source of halogen atoms from N_2O_5 chemistry but also for polar halogen activation chemistry, generally. That N_2O_5 reactions on halide-doped ice systems produce halogen atom precursors at high yield should be explored in models of Arctic chemistry, especially for springtime conditions in the presence of nitrate and halide containing snowpacks where sunlight-driven emission of NO_x from the snowpacks will lead to N_2O_5 formation above and within the snowpack during night and perhaps during the day depending the exact chemical and radiation fields. Our results are also likely applicable to salty snow and ice surfaces located in mid-latitude urban areas where higher levels of NO_x are present and the deposition of N_2O_5 to such surfaces could present a persistent wintertime source of chlorine atoms even in continental regions.

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