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Uptake and reaction of HOBr on frozen and dry NaCl/NaBr surfaces between 253 and 233 K

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Abstract. The uptake and reaction of HOBr with frozen salt surfaces of variable NaCl / NaBr composition and temperature were investigated with a coated wall flow tube reactor coupled to a mass spectrometer for gas-phase analysis. HOBr is efficiently taken up onto the frozen surfaces at temperatures between 253 and 233 K where it reacts to form the di-halogens BrCl and Br_2, which are subsequently released into the gas-phase. The uptake coefficient for HOBr reacting with a frozen, mixed salt surface of similar composition to sea-spray was $\approx 10^{-2}$. The relative concentration of BrCl and Br_2 released to the gas-phase was found to be strongly dependent on the ratio of Cl^- to Br^- in the solution prior to freezing / drying. For a mixed salt surface of similar composition to sea-spray the major product at low conversion of surface reactants (i.e. Br^- and Cl^-) was Br_2.

Variation of the pH of the NaCl / NaBr solution used to prepare the frozen surfaces was found to have no significant influence on the results. The observations are explained in terms of initial formation of BrCl in a surface reaction of HOBr with Cl^-, and conversion of BrCl to Br_2 via reaction of surface Br^-. Experiments on the uptake and reaction of BrCl with frozen NaCl / NaBr solutions served to confirm this hypothesis. The kinetics and products of the interactions of BrCl, Br_2 and Cl_2 with frozen salt surfaces were also investigated, and lower limits to the uptake coefficients of > 0.034, > 0.025 and > 0.028 respectively, were obtained. The uptake and reaction of HOBr on dry salt surfaces was also investigated and the results closely resemble those obtained for frozen surfaces. During the course of this study the gas diffusion coefficients of HOBr in He and H_2O were also measured as (273 ± 1) Torr cm^2 s^{-1} and (51 ± 1) Torr cm^2 s^{-1}, respectively, at 255 K. The implications of these results for modelling the chemistry of the Arctic boundary layer in springtime are discussed.

1 Introduction

Field measurements have conclusively shown that the episodic, catalytic destruction of ozone in the polar tropospheric boundary layer is strongly correlated with the presence of reactive bromine compounds (Barrie et al., 1988, 1994; Barrie and Platt, 1997). Time resolved measurement of the concentrations of alkanes, alkenes and alkynes (Jobson et al., 1994; Ramacher et al., 1997, 1999; Rudolph et al., 1999; Boudries and Bottenheim, 2000), detection of photo-labile bromine compounds such as HOBr, BrCl and Br_2 (Impey et al., 1997, 1999; Foster et al., 2001), the direct measurement of the BrO radical in ground-based experiments (Hausmann and Platt, 1994; Miller et al., 1997; Tuckermann et al., 1997), and by satellite (Chance, 1998), measurement of active chlorine via chemical amplification (Perner et al., 1999) and isotopic studies of CO (Röckmann et al., 1999) provide the experimental evidence for the presence of reactive, gas-phase bromine and chlorine species and indicate their central role in ozone destruction in several arctic locations (Oltmans, 1981; Barrie et al., 1988; Oltmans et al., 1989; Anlauf et al., 1994; Solberg et al., 1996; Lorenzen-Schmidt et al., 1998). Measurements in the Antarctic indicate that bromine catalysed ozone loss can take place even in this relatively pristine environment (Kreher et al., 1997; Wessel et al., 1998).

The chemical mechanism(s) by which high concentrations of reactive bromine and chlorine compounds are sustained are not yet completely characterised although an important role for heterogeneous reactions of HOBr (Fan and Jacob, 1992; McConnell et al., 1992; Mozurkewich, 1995; Tang and McConnell, 1996) has been identified.

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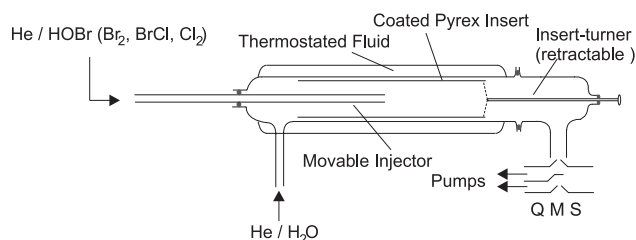(Crowley@mpch-mainz.mpg.de)

Fig. 1. Schematic Diagram of the experimental set-up. QMS = Quadrupole Mass Spectrometer.

In a recent publication (Fickert et al., 1999) we were able to show that the interaction of HOBr with aqueous NaCl / NaBr solutions of similar composition to sea-spray was an efficient source of Br_2 (and BrCl) if the solution pH was less than ≈ 6. The uptake coefficient (see below) for the interaction of HOBr with salt containing deliquescent aerosols has been shown to be large (Abbatt and Waschewsky, 1998). The initial step is thought to be an acid catalysed reaction between HOBr and Cl^-:

$$HOBr + Cl^- + H^+ \rightleftharpoons BrCl + H_2O \qquad (1)$$
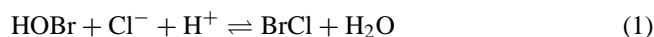
Rapid, aqueous phase equilibria result in the conversion of BrCl to Br_2,

$$BrCl + Br^- + H^+ \rightleftharpoons Br_2 + HCl \qquad (2)$$

and the relative concentration of Br_2 and BrCl released to the gas-phase is controlled by aqueous phase equilibrium reactions of Br_2Cl^- (Wang et al., 1994; Fickert et al., 1999). Only when the $[Br^-]$ / $[Cl^-]$ ratio was very low compared to the composition of sea-water, was BrCl released in significant yield.

In the present study we investigate the efficiency of di-halogen release from the interaction of HOBr with frozen salt surfaces that mimic the arctic snow/ice pack. Supplementary experiments that examined the uptake and reaction of HOBr on "dry" surfaces and the uptake and reaction of molecular di-halogens with frozen surfaces were also carried out to gain insight into the parameters that control the rate and mechanism of the chemical interaction. Surprisingly, with few exceptions, the results from this work represent the first measurements of the kinetics and mechanisms of the reactions of halogenated species on mixed Cl^- / Br^- surfaces made from aqueous solutions that were of similar composition to atmospheric sea-spray /sea-water.

2 Experimental

2.1 Flow tube and mass spectrometer

The uptake and reaction of the halogen trace gases on frozen and dry surfaces was investigated using a coated wall flow tube (Fig. 1) combined with a differentially pumped quadrupole mass spectrometer (Holmes et al., 2001). The flow tube set up consists of a horizontally mounted Pyrex glass tube (length 300 mm, internal diameter 27.5 mm) with a thermostatted jacket to regulate the temperature. The surfaces of interest are coated onto the inner wall of a snug-fitting Pyrex insert ($l = 210$ mm, $id = 25.5$ mm), located in the centre of the flow tube. The experiments were conducted at total (flow tube) pressures of between 0.75 and 3 Torr He (1 Torr = 1.333 hPa), the temperature was varied between 233 and 253 K. The bulk flow rate of He through the flow tube was between 400 and 1000, standard cm^3 min^{-1}, resulting in linear velocities of between 300 and 1500 cm s^{-1}. Reactive trace gases, diluted in He, were introduced into the flow tube via a movable injector, the translation of which enabled the contact time between trace gas and surface to be varied. When appropriate, the main gas flow, which entered the flow-tube through a sidearm of the reactor, was humidified to prevent evaporation of the frozen surface. Trace gases were analysed with a quadrupole mass spectrometer (QMS), equipped with an electron-impact ion source (Fickert et al., 1998). HOBr, BrCl and Br_2 were monitored at their parent ions ($m/z = 96$, 116 and 158, respectively).

2.2 Surface preparation, chemicals

In order to prepare reproducible frozen surfaces the following methodology was adopted. The Pyrex insert was cleaned using a dilute HF solution before thorough rinsing with distilled water and the aqueous solution from which the frozen or dry surfaces were to be made. Following this, a few ml of the same solution was introduced between two Teflon constraining rings. By slowly turning the insert, a film of estimated thickness $\approx 100 \mu m$ was evenly distributed on the glass walls. The insert was then placed into the pre-cooled flow tube where a translucent, frozen film was formed within a few seconds. The insert could also be slowly turned during the freezing process. Once the flow tube was re-sealed the bulk gas flows, at the correct humidity to maintain the ice film in equilibrium with gas-phase, were established. Inspection of the NaCl phase diagram (Koop et al., 2000) shows that at temperatures below 251 K (the temperature of the ice/liquid/NaCl·$2H_2O$ eutectic), only ice and NaCl dihydrate co-exist. The presence of bromide ions at concentrations of 10^{-3} M is not expected to modify this significantly and, for the majority of our experiments, there is not expected to be an aqueous phase in equilibrium with the bulk material of the substrate.

When dry films were required, the frozen film was exposed to dry He as the temperature was allowed to increase slowly to room temperature over a period of ≈ 30 min. In this way an even, unbroken, dry salt surface could be reproducibly obtained. In the text we refer to these surfaces as "dry" although the relative humidity was also varied in these experiments. HOBr was prepared by the reaction of $AgNO_3$ with Br_2 in solution as described previously (Fickert et al., 1999), and
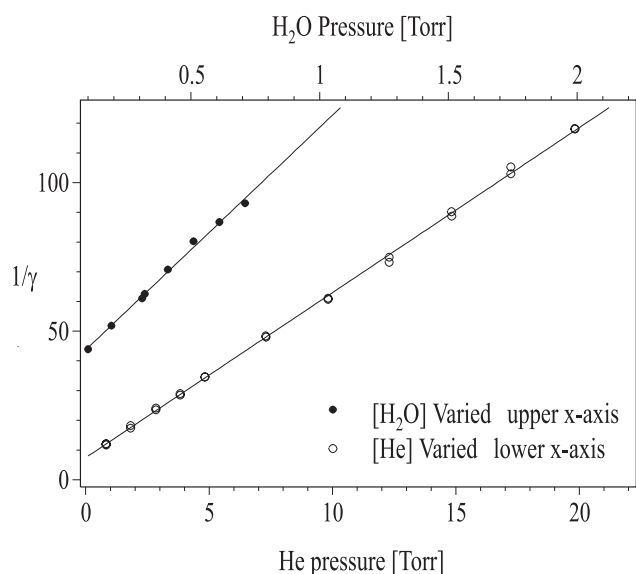
Fig. 2. Plot of inverse uptake coefficient of HOBr vs. pressure of He or H₂O, for dry salt and HCl doped Pyrex surfaces at 253 K. Diffusion coefficients and accommodation coefficients may be extracted from the gradients and intercepts of these lines. (See Eq. iii in text)

was stored as an aqueous solution at $\approx -30°C$. BrCl was prepared by allowing a Br_2 / Cl_2 mixture to come to equilibrium in a blacked glass storage bulb, and its mixing ratio determined by absorption spectroscopy. The response of the mass spectrometer was calibrated against known concentrations of Br_2, Cl_2 and BrCl, and was determined over a range of flow-tube pressures, gas-phase water concentrations and instrument configurations. The mass spectrometer signals of HOBr were converted to concentrations by assuming 100% yield of Br_2 in the reaction of HOBr with aqueous, acidified, bromide containing solutions (Fickert et al., 1999).

The aqueous bromide / chloride solutions were prepared from analysis grade NaCl and NaBr and de-ionised water. For most experiments the solutions were 2 M NaCl and 3×10^{-3} M NaBr. The Cl^- to Br^- ratio (≈ 660) is thus the same as found in sea-water, and the concentrations similar to those expected to be present in sea-spray (Sander and Crutzen, 1996). The pH of un-buffered solutions was 5.5 unless this parameter was deliberately manipulated. In addition, solutions of varied Cl^- to Br^- ratio, and also pure Cl^- and Br^- solutions were used.

2.3   Determination of uptake coefficients

In the present experiments, the pseudo first-order rate coefficient for loss to the reactive surface k_w was calculated from the variation of signal with injector position according to:

$$[C]_{z_2} = [C]_{z_1} \cdot \exp\left(-k_w \cdot \frac{\Delta z}{v}\right) \qquad (i)$$

where $[C]_{z_{1,2}}$ is the trace gas concentrations at injector positions z_1 and z_2, Δz represents the distance between the positions z_1 and z_2 and v is the gas flow velocity in the tube. The ratio $\Delta z/v$ thus defines the gas-surface contact time. The measured value of k_w has to be corrected (to give k_{cor}) to take into account radial concentration gradients caused by efficient interaction of the trace gas at the wall (Brown, 1978). This required knowledge of the diffusion coefficients of HOBr in both He and H_2O, which were determined separately (see results). The uptake coefficient, γ, was then obtained directly from k_{cor} (Howard, 1979):

$$\gamma = \frac{2 \cdot r \cdot k_{cor}}{\omega} \qquad (ii)$$

where r is the internal radius of the coated glass insert, and ω is the mean molecular velocity of the trace gas, derived from the Boltzmann equation. Note that using this method, we make the assumption that the geometric surface area of the ice substrate is appropriate for calculating the uptake coefficient, though there is still some controversy regarding this (Hanson and Ravishankara, 1993; Keyser et al., 1993). Corrections based on pore diffusion calculations have only been properly tested for ice surfaces that were formed by condensation from the gas-phase, which are considerably rougher than those formed from the relatively slow freezing of a liquid as practised here. We expect that our ice surfaces, which appear smooth and translucent to the eye, are significantly less porous that those grown by vapour deposition.

3   Results and discussion

3.1   Diffusion coefficients of HOBr in He and H₂O

Experiments to determine the diffusion coefficient of HOBr in water vapour, $D_{H_2O}^{HOBr}$, were carried out using a salt surface doped with HCl at 255 K. For this measurement, the He gas flow was accurately humidified, and the uptake of HOBr, limited by its diffusion through both He and H_2O, was monitored. The diffusion coefficient of HOBr in He, D_{He}^{HOBr}, was also determined using the reaction with HCl on the surface of the glass insert. In these experiments, HCl was added to the bulk gas flow, and was present at a concentration in excess of HOBr by more than a factor of 10.

For diffusion-limited uptake onto the surface of a reactor with cylindrical geometry, the equation approximating the dependence of the uptake coefficient on the bath gas pressure is given by: (Hanson et al., 1992)

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{\omega \cdot r \cdot P_{H_2O}}{7.32 \cdot D_{H_2O}} + \frac{\omega \cdot r}{7.32 \cdot D_{He}} \cdot P_{He} \qquad (iii)$$

This assumes that reaction at the surface is rapid and not rate limiting. Doping the ice / glass surface with excess HCl ensures that this is the case (Abbatt, 1994).

Figure 2 (open circles) shows plots of $1/\gamma$ vs. He bath gas pressure for uptake onto a sea-salt substrate in the presence
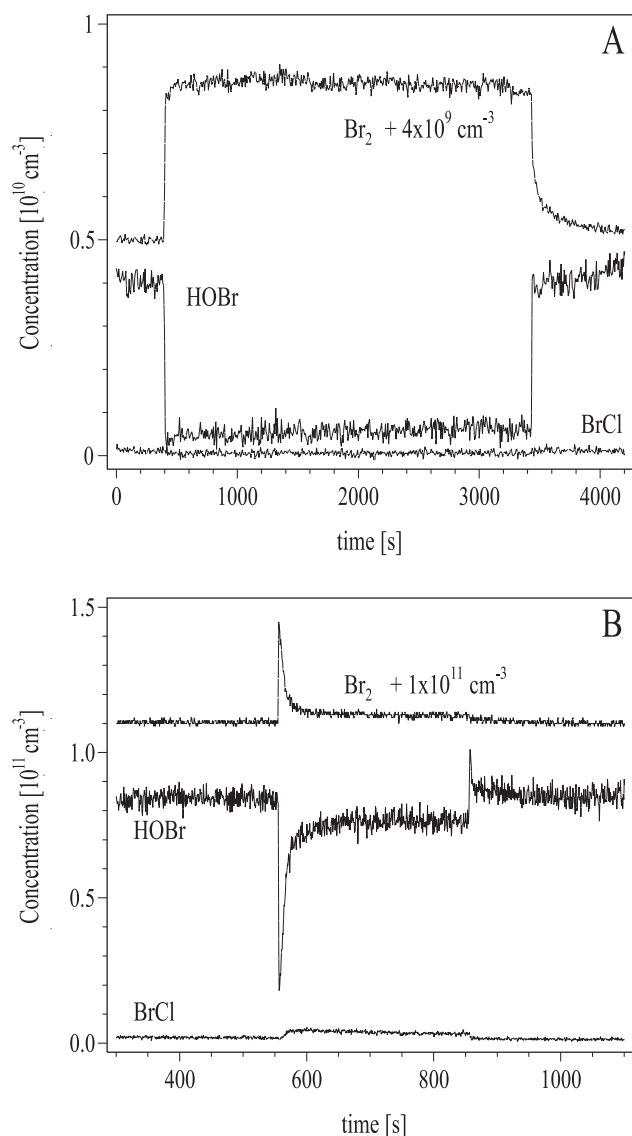
Fig. 3. Uptake of HOBr and subsequent product formation, on a frozen mixed salt surface at 233 K. **(a)** $[HOBr]_{init} = 4 \times 10^9$ molecules cm^{-3}, exposure of the surface to HOBr begins at 400 s when the injector is retracted. **(b)** $[HOBr]_{init} = 8.5 \times 10^{10}$ molecules cm^{-3}, exposure of the surface to HOBr begins at 550 s. In both cases, the Br_2 trace has been offset for clarity of presentation.

of excess HCl at 255 K. Two experiments were performed at each pressure, though the excellent reproducibility makes some data points difficult to see. During these experiments the water vapour pressure was held constant at ca. 0.8 Torr. The linear dependence of the inverse uptake coefficient on the pressure of the He bath gas enabled the diffusion coefficient to be extracted from the gradient (see Eq. iii above). The diffusion coefficient at 255 K was found to be $D_{He}^{HOBr} = (273 \pm 1)$ Torr cm^2 s^{-1}, where the errors are precision only

(2σ). This result can be compared to the only previous experimental determination of $D_{He}^{HOBr} = (319 \pm 48)$ Torr cm^2 s^{-1} at 274 K. Assuming a $T^{1.75}$ dependence on temperature, this indicates a value of (281 ± 42) Torr cm^2 s^{-1} at 255 K, in good agreement with the present result. These values are in accord with diffusion coefficient calculations based on average collision diameters and Lennard-Jones potentials (Wachsmuth et al., 2002)

A separate set of experiments (filled circles) was performed in which the diffusion limited uptake of HOBr onto frozen sea-salt surfaces and excess HCl in the presence of various pressures of added water vapour was studied. During these experiments the He pressure was held constant at 2 Torr. Each data point represents the average of at least three uptake experiments. The slope of this data set yields a diffusion coefficient of $D_{H_2O}^{HOBr} = (51 \pm 1)$ Torr cm^2 s^{-1} where the errors are precision only (2σ). This is the first direct determination of this quantity. The data taken with the partially humidified sea-salt surface (open circles) was analysed to obtain the y-axis intercept of the data. Once the contribution from the diffusion of HOBr in water (see Eq. iii) was subtracted, an estimate of the mass accommodation coefficient for uptake of HOBr onto frozen, HCl doped, sea-salt surfaces can be calculated. A value of $\alpha \approx 0.15$ was obtained, which is comparable to the literature value of $\gamma = 0.25$, obtained for the uptake of HOBr onto ice doped with HCl (Abbatt, 1994).

3.2 HOBr uptake onto frozen salt surfaces: product formation

The uptake and reaction of HOBr on frozen salt substrates was examined at a variety of temperatures between 233 and 253 K, at various NaBr / NaCl concentration ratios and with variation of the initial HOBr concentration and total pressure. For each experiment a fresh substrate was used.

Figure 3a displays raw data obtained at 233 K with an initial (aqueous) composition of the salt of 2 M NaCl and 3×10^{-3} M NaBr. After a steady flow of HOBr at a concentration of $\approx 4 \times 10^9$ cm^{-3} has been established ($t = 0$ to $t = 400$ s, constant mass spectrometer signal at $m/z = 96$) the injector is withdrawn and the HOBr is exposed to a well defined area of frozen substrate. At this point, the HOBr signal drops precipitously, indicating uptake onto the substrate, and the molecular ion of Br_2 is, within the time resolution of the measurement, instantaneously observed. The uptake of HOBr and the release of Br_2 proceeds at approximately the same rate until $t = 3400$ s, during which the HOBr is seen to be converted stoichiometrically to Br_2. When the injector is re-inserted at $t \approx 3400$ s, and contact between HOBr and the substrate is stopped the HOBr signal returns to its initial value, and Br_2 production ceases. We note that although the result shown is representative of several data sets, the exact shape of the HOBr uptake profile was somewhat variable from one experiment to the next, though the size of

the initial uptake coefficient (directly after the injector was withdrawn) was reasonably constant. Despite efforts made to generate surfaces in a reproducible manner, this effect probably reflects differences in surface characteristics such as the number of defect sites and porosity, which will influence the availability of reactive sites on the surface. As shown, there is no evidence for significant production of BrCl in this experiment. In a second experiment, at the same temperature (Fig. 3b), a fresh substrate was exposed to a significantly higher concentration of HOBr (8.5×10^{10} cm^{-3}). At this concentration of HOBr the time dependence of its uptake is markedly different. Following an initially large uptake directly after the injector has been withdrawn ($t = 550$ s) the concentration of HOBr increases rapidly until it almost reaches its original level. At the same time Br$_2$ is initially formed at high yield, but decreases in concentration as the uptake of HOBr slows down. In this experiment BrCl is also clearly formed, though there is a delay of ≈ 50 s before its maximum concentration is reached. An examination of the HOBr, Br$_2$ and BrCl profiles at $600 < t < 850$ s shows that HOBr is being converted to Br$_2$ and BrCl in roughly equal amounts.

The change in the HOBr uptake profile as the HOBr concentration is varied indicates that, at higher concentrations, there is sufficient HOBr to modify the reactivity of the surface on the time scales of these experiments, i.e. reactive sites on the surface are depleted as the reaction progresses, and both the uptake of HOBr and the formation of products decrease with time. An important aspect of these results is the switch in products from only Br$_2$ at low HOBr to Br$_2$ and BrCl as the concentration of HOBr is increased.

In a further series of experiments, the dependence of the HOBr uptake and the formation of Br$_2$ and BrCl products was examined as a function of the initial ratio of Br$^-$ to Cl$^-$ in the aqueous solution. NaCl was always kept at 2 M, whilst NaBr was varied between 3×10^{-3} and 3×10^{-5} M. The data from an experiment with NaBr $= 3 \times 10^{-4}$ M carried out at 233 K is displayed in Fig. 4. When compared to the results of Fig. 3a, the decrease of the NaBr concentration from 3×10^{-3} to 3×10^{-4} M is seen to have a profound impact on the time dependence of the HOBr uptake and release of products, and also on the identity of the products. At the lower NaBr concentration of $= 3 \times 10^{-4}$ M the uptake of HOBr is characterised by a rapid decrease in γ from its initial value over a period of ≈ 50 s, followed by a phase in which the uptake decreases slowly over several hundred seconds. At the same time, the Br$_2$ formation curve is also "spiked" and a significant amount of BrCl is formed, again with a delay period before it is detected. The ratio of BrCl to Br$_2$ formed at short exposure times is clearly significantly higher than in experiments with 3×10^{-3} M Br$^-$. For comparison, the results from experiments in which HOBr was reacted with pure NaCl and NaBr surfaces are shown in Fig. 5. Figure 5a shows the uptake of HOBr onto frozen chloride (initial concentration 2 M). The uptake was strongly time dependent in
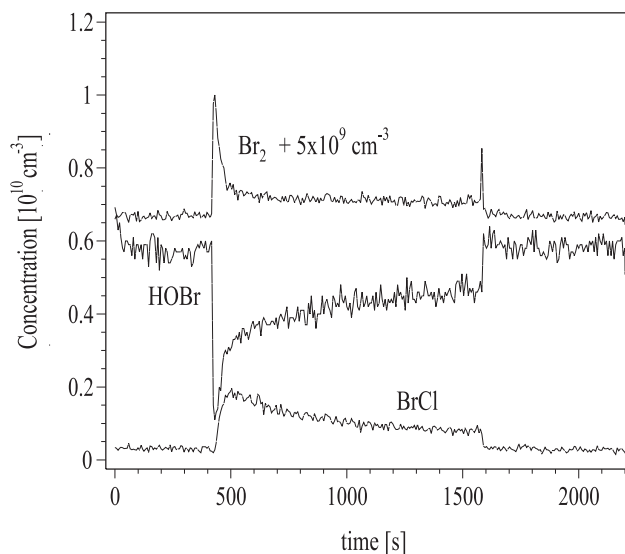

Fig. 4. Uptake of HOBr onto a frozen (233 K) mixed salt surfaces made from an aqueous solution of composition 2 M NaCl, 3×10^{-4} NaBr. The Br$_2$ trace has been offset for clarity of presentation.

all experiments, irrespective of the initial HOBr concentration. At low HOBr concentrations ($< 1 \times 10^{10}$ cm^{-3}), the only product observed was BrCl, the release of which was not instantaneous, but took > 100 s to reach a maximum value. The yield of BrCl (per HOBr taken up) was constant at 0.5 ± 0.1 after this maximum was passed, implying the presence of non-reactive sites for HOBr uptake. At higher initial concentrations of HOBr, Br$_2$O was often formed on the chloride ice surface, via the reaction.

$$HOBr + HOBr \rightleftharpoons Br_2O + H_2O \qquad (3)$$
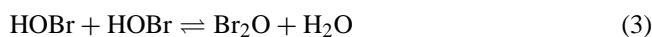
Br$_2$O was monitored at $m/z = 176$. The Br$_2$O formation was found to be dependent on the temperature of the flow tube, with enhanced formation at low temperatures. By measuring the relative HOBr and Br$_2$O signals at various temperatures it was possible to set up simultaneous equations and determine the sensitivity of the mass spectrometer to Br$_2$O. When high concentrations of HOBr were present, the product (BrCl and Br$_2$O) to reactant ratio was ≈ 1 initially, falling to 0.4 ± 0.1 at longer times. Figure 5b shows the uptake of HOBr onto frozen bromide (initial concentration 3×10^{-3} M). In this case instantaneously released Br$_2$ was the only product, with a constant yield of 0.9 ± 0.1 per HOBr taken up.

The above observations of HOBr uptake, Br$_2$ and BrCl formation, and the dependence of these on the initial HOBr concentration or the ratio of NaBr to NaCl are used to derive a qualitative description of the reactions taking place on the frozen substrate. In a first step we expect HOBr to react on the surface with either Cl$^-$ or Br$^-$ to form either BrCl or Br$_2$:
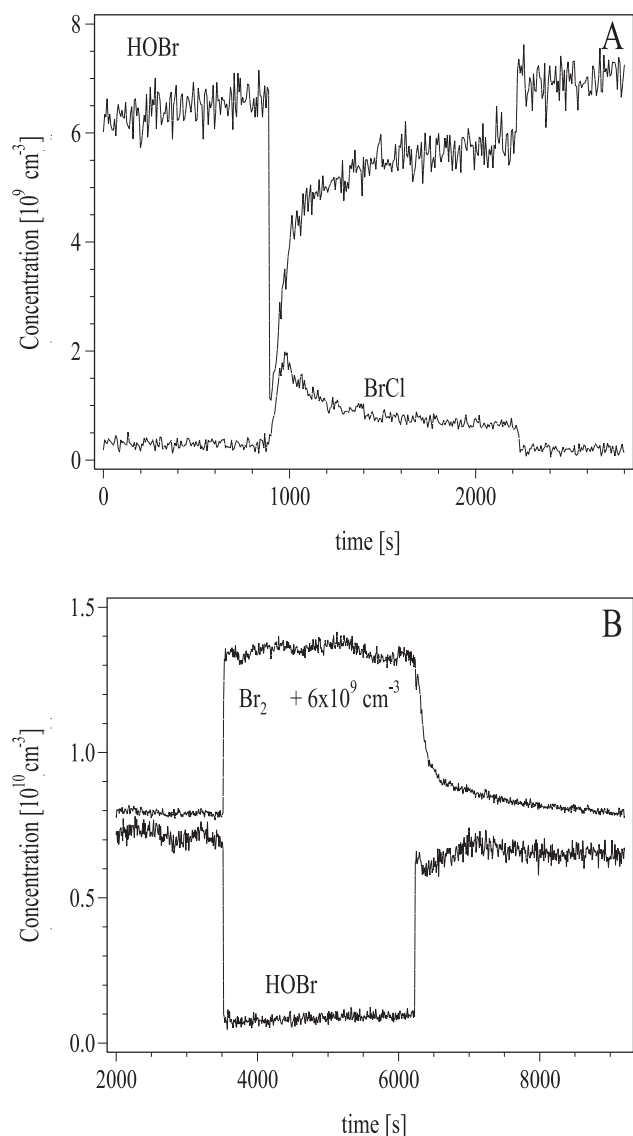
$$HOBr + Br^- \rightleftharpoons Br_2 + OH^- \qquad (4)$$
$$HOBr + Cl^- \rightleftharpoons BrCl + OH^- \qquad (5)$$
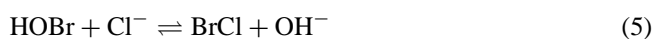
Fig. 5. Uptake of HOBr onto frozen salt surfaces. **(a)** 2 M NaCl, T = 233 K, **(b)** 3×10^{-3} M NaBr, 243 K. The Br_2 trace has been offset for clarity of presentation.

Due to its greater polarity, we expect BrCl to have a relatively long residence time on the surface compared to Br_2, thus, when sufficient Br^- is available on the surface for reaction, BrCl will be converted to Br_2 before it can leave the surface to be detected as a gas-phase species.

$$BrCl + Br^- \rightleftharpoons Br_2 + Cl^- \qquad (6)$$

When the Br^- concentration is lowered, the rate of desorption of BrCl from the surface becomes comparable with the rate of its surface reaction with Br^- and some will be detected, with a delay period due to retention on the surface. When Br^- is low, BrCl may thus build up on the surface so that the increased flux through the back Reaction (5) results in the net decrease in HOBr uptake between

$500 < t < 1500$ s seen in Fig. 4. This effect may be further enhanced by occupation of reactive sites by BrCl. The same mechanism also explains the formation of both BrCl and Br_2 when high initial HOBr concentrations are employed. In this case, the surface Br^- is rapidly depleted by the BrCl + Br^- reaction (Fig. 3b, $550 < t < 600$ s), and further uptake of HOBr can result in BrCl formation and release. Independent evidence for an efficient conversion of BrCl to Br^- on frozen NaCl / NaBr substrates was gained in a separate set of experiments that directly examined the uptake of BrCl (see below).

Until now the formation of Br_2 following reaction of HOBr with mixed salt surfaces has been discussed largely in terms of an indirect mechanism in via formation of BrCl reaction. This is due to the greater concentration of Cl^- compared to Br^- in the aqueous solutions used to generate the frozen surfaces, which favours Reaction (5) over Reaction (4). The rate of each reaction will however depend on its rate coefficient and the surface concentration of the halide ions. In the aqueous phase the reaction of HOBr with Br^- is a factor of ≈ 3 larger than that for HOBr with Cl^- which alone cannot compensate the factor 660 in the relative concentration of Cl^- and Br^- in the bulk solutions. However, during the freezing process, which presumably starts at the surface of the cold glass insert and proceeds outwards towards the gas-liquid interface, some separation of Br^- and Cl^- will be caused by the higher solubility of Br^- compared to Cl^-. This will result in a frozen film that has a higher surface Br^- / Cl^- ratio compared to bulk. Observations of enhanced Br^- / Cl^- concentration ratios at the surface have been made on NaBr / NaCl crystals grown from aqueous solutions (Zangmeister et al., 2001), and from a melt (Ghosal et al., 2000). In the present experiments, although a surface enhancement of the Br^- ion concentration probably occurs, we have no means to determine its extent, but note that even a surface enhancement of a factor of 10 in the Br^- / Cl^- ratio would increase the contribution of Reaction (5) to just $\approx 5\%$ if the relative aqueous phase rate coefficients for these reactions are applicable.

The observations presented here appear to be completely consistent with the known aqueous-phase equilibrium chemistry involved in the uptake and reaction of HOBr on deliquescent sea-salt aerosols or solutions (Wang et al., 1994; Fickert et al., 1999) and despite contrary indications from the phase-diagram, it is tempting to suggest that the reactions are taking place in aqueous medium. However, an important aspect of the aqueous phase transformation of HOBr into Br_2 or BrCl is the requirement of low pH (Abbatt and Waschewsky, 1998; Fickert et al., 1999) as the reactions are acid catalysed (Wang et al., 1994). We have shown (Fickert et al., 1999) that the release of molecular halogens from aqueous solutions is suppressed at a pH of greater that ≈ 7, and have therefore carried out a series of experiments in which the NaBr / NaCl solutions were adjusted in pH between 4 and 10 prior to freezing. It was found that the variation of pH had no influence on identity of the products or their yields per HOBr taken

up to the surface. As the amount of liquid-phase available at the surface of a frozen sample will depend on the temperature, we also carried out experiments at various temperatures between 233 and 253 K. Again, no significant change in the uptake coefficient, time dependence or product distribution (i.e. the Br_2 to BrCl ratio) was observed over this temperature range. Even in those experiments where the temperature was above the eutectic for NaCl (i.e. at 253 K) there was no obvious change in either the kinetics of the uptake process or the product distribution.

3.3 Uptake of HOBr to frozen surfaces: surface capacity

Even at high HOBr our experiments did not reveal complete deactivation (i.e. titration of reactive sites). Despite this, some indication of the capacity of the surface to remove HOBr can be derived from the data in, e.g. Figs. 3 and 4. In Fig. 4, (NaCl = 2M, NaBr = 3×10^{-4} M), during the exposure phase ($t \sim 450 - 1500$ s) approximately 1×10^{16} HOBr have been lost from the gas-phase due to contact with ~ 80 cm^2 of the frozen surface, yielding a lower limit to the capacity of the frozen surface to remove HOBr of 1×10^{14} per cm^2. In contrast, in Fig. 3a (NaCl = 2M, NaBr = 3×10^{-3} M) $\sim 5 \times 10^{14}$ HOBr are taken up per cm^2 (and converted to Br_2) with no significant change in the rate of reaction over the exposure period. Again, this is different to the result in Fig. 3b in which much higher fluxes of HOBr to the same surface result in a deactivation of the surface after just 50 s in which $\sim 1.5 \times 10^{14}$ HOBr were taken up. This indicates that the capacity of the surface to support reaction can depend on the rate of reactivation, perhaps due to surface reorganisation. Note that reactivation of the surfaces, which are quite dynamic at these temperatures, has previously been documented by Holmes et al. (2001) in studies of HOI and $IONO_2$ uptake.

Those experiments in which the pH of the aqueous solution used to generate the frozen substrate was varied show that the capacity of the surface of convert HOBr to BrCl or Br_2 was not influenced by this parameter. Indeed, at a pH of 10, the amount of HOBr taken up to the frozen surface and converted to di-halogen can exceed the number of H^+ initially present in the entire sample by orders of magnitude. In contrast to the aqueous phase, the surface reaction is clearly not driven by the presence of protons.

3.4 HOBr uptake onto frozen salt surfaces: uptake coefficients

As shown in, e.g. Fig. 3b, the uptake of HOBr onto a frozen, mixed salt surface is sometimes time dependent, with an initially large uptake coefficient that decreases with exposure time due to the deactivation of reactive surface sites. At low concentrations of HOBr and sufficiently high halide ion concentrations the uptake was independent of exposure time on the time scales of a typical experiment (e.g. Fig. 3a). In order

Table 1. Summary of kinetic and product data obtained for HOBr uptake onto frozen salt surfaces

$[Cl^-]$ / M	$[Br^-]$ / M	T K	Major Products*	γ_{init}	n
2	3×10^{-3}	248	Br_2	0.026 ± 0.006	10
2	3×10^{-3}	233	Br_2	0.032 ± 0.009	16
2	3×10^{-3}	253	Br_2	0.012 ± 0.005	2
2	3×10^{-3}	243	Br_2	0.017 ± 0.09	6
2	0	233	BrCl	0.043 ± 0.008	3
2	0	248	BrCl	0.016 ± 0.007	2
0	0.1	248	Br_2	> 0.01	1
0	3×10^{-3}	248	Br_2	0.036	1

*Product formed at short exposure times. The evolution of the product distribution as a function of reaction time is described in the text. n = number of experiments.

to make meaningful comparison of uptake coefficients from different data sets, the uptake coefficient shortly after exposure, γ_{init}, is reported. The initial uptake coefficients listed have been corrected for radial concentrations gradients as described in the experimental section. Only those data where the criterion $k_{cor} \leq 4k_{obs}$ is fulfilled are reported/displayed as absolute values, otherwise a lower limit to γ_{init} is presented. One set of experiments was carried out to examine the effect of temperature on the initial uptake coefficient of HOBr to a mixed salt surface, whereby uptake coefficients were obtained at temperatures of 233, 243, 248 and 253 K, with the 2 M Cl^- / 3×10^{-3} M Br^- surfaces. The results are presented in Table 1, and plotted in Fig. 6 (solid circles). The data points are averages from several experiments. Although the data are associated with some scatter (the errors bars represent reproducibility) there is a trend of increasing uptake coefficient with decreasing temperature. Also plotted with this data are results obtained using the same initial Cl^- concentration, but without bromide present (open circles). The initial uptake coefficients are, within error limits, indistinguishable from those with 3×10^{-3} M bromide, and clearly, at these concentrations, the presence of bromide on the surface has little influence on the magnitude of the HOBr uptake coefficient. This substantiates the arguments presented above that the initial step is the reaction of surface adsorbed HOBr with the dominant halide ion, Cl^-, rather than reaction with Br^-. Uptake coefficients were also obtained for the reaction of HOBr with a surface prepared from freezing NaBr solutions of either 3×10^{-3} or 0.1 M concentration.
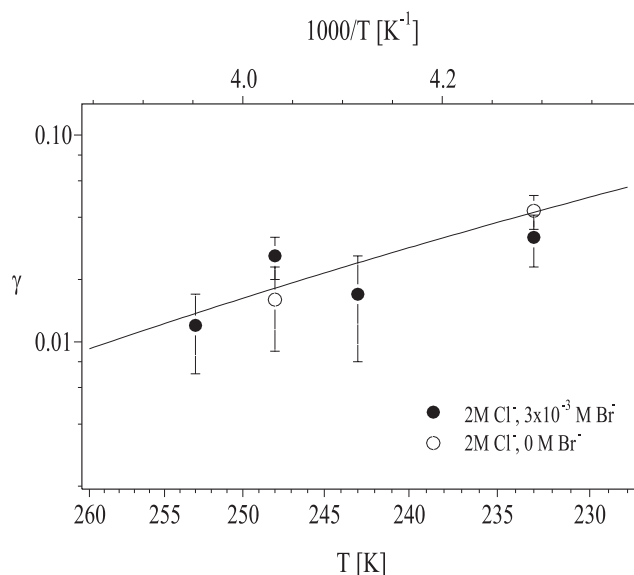
Fig. 6. Temperature dependence of the initial uptake coefficient of HOBr onto frozen surfaces made from solutions containing 2 M NaCl with and without added NaBr. The error bars define the reproducibility of the result.

Fig. 7. Uptake of BrCl and Cl_2 onto a mixed, frozen salt surface and formation of Br_2. $T = 233$ K, 2 M NaCl, 3×10^{-3} M NaBr. The Br_2 and Cl_2 traces have been offset for clarity of presentation.

3.5   BrCl, Br_2 and Cl_2 uptake onto frozen salt surfaces

The uptake of HOBr and release of Br_2 is described above in terms of formation of BrCl in a primary step, followed by reaction of BrCl on the surface with Br^-. This concept was tested in separate experiments by measuring the uptake of BrCl, Br_2 and also Cl_2 onto frozen salt surfaces of varying composition. Representative data from an experiment to examine the uptake of BrCl (plus Br_2 and Cl_2 impurity) on a mixed Br^- / Cl^- surface are shown in Fig. 7, which shows that BrCl is taken up efficiently and that the increase in gas-phase Br_2 is approximately equal to the summed loss of BrCl and Cl_2 from the gas-phase. If the initial Cl^- to Br^- ratio is close to 660 as found in sea-water, BrCl will react on the surface to form Br_2. A lower limit to the uptake coefficient of 0.034 was obtained at 233 K.

In a further set of experiments the uptake of Br_2 onto mixed salt surfaces was examined. Br_2 was found to react strongly with these surfaces in halogen inter-conversion reactions. Although BrCl is expected to be the primary product, it reacts with the surface bromide to form Br_2. The uptake coefficient was determined to be > 0.025 at 233 K. On pure bromide at 243 K, Br_2 is both taken up to react with the surface ($\gamma > 0.01$) and released to form a different Br_2 molecule. In this case, the use of isotopically labelled NaBr was used to discriminate between the reactant and product Br_2.

The uptake of Cl_2 was examined on mixed salt surfaces at 233 K, and resulted in the stoichiometric formation of Br_2, presumably via the intermediacy of BrCl. A lower limit to
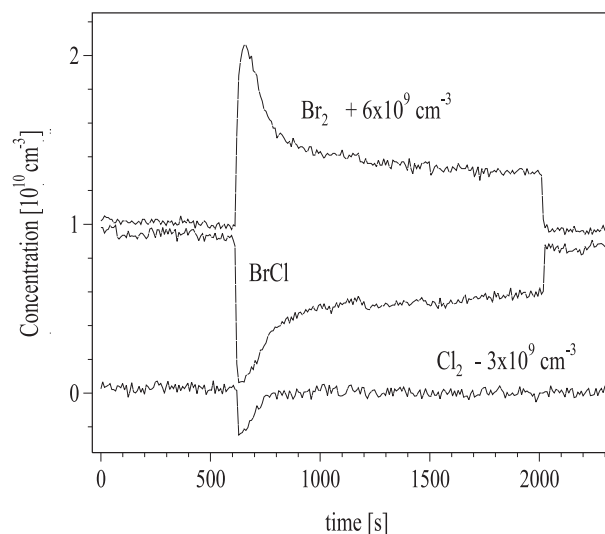
the uptake coefficients of > 0.028 was obtained. These results are summarised in Table 2.

3.6   HOBr uptake onto dry salt surfaces

Experiments to examine the uptake of HOBr onto dry surfaces were performed on both mixed Br^- / Cl^- surfaces and pure Cl^- surfaces, and at various relative humidities. For the mixed salt at 243 K (see Fig. 8a), γ was found to be 2×10^{-2} and time independent. Uptake onto the pure Cl^- surface (see Fig. 8b) behaved differently and was clearly time dependent, with an initial uptake coefficient of 6×10^{-2} that decreased to a steady value of $\approx 3 \times 10^{-3}$ after ≈ 500 s. BrCl was formed at high yield ($\approx 70\%$), but not stoichiometrically. Upon re-inserting the injector ($t \approx 2050$ s) some HOBr was released from the surface to the gas-phase, indicating the presence of unreactive, physi-adsorption sites on the chemically aged surface, and explaining the observation that the yield of BrCl per HOBr lost from the gas-phase was not 100%. Similar to the uptake of HOBr onto frozen surfaces, the uptake onto dried and humidified surfaces resulted in the release of both Br_2 and trace amounts of BrCl, with Br_2 the major initial product released to the gas-phase, followed by BrCl release as the surface bromide was depleted. There was no change in the product distribution as the relative humidity was varied between 0 and 100%. Note that the deliquescence relative humidities of NaCl at 298 K is 75.6% and shows a weak temperature dependence, increasing to $\sim 76\%$ at 273 K (Tang and Munkelwitz, 1993), that of NaBr is about 58% at 298 K (Malvestuto and Ascoli, 2001). These results are summarised in Table 2.

3.7 Comparison with literature

3.7.1 HOBr uptake to frozen and dry surfaces

The present results pertaining to the uptake and reaction of HOBr on frozen salt surfaces can be directly compared to the similar but less extensive studies of Kirchner et al. (1997). Also using a flow-tube / mass spectrometer set-up, those authors found that the reaction of HOBr on a frozen, mixed NaCl / NaBr surface at 233 K resulted in the release to the gas-phase of both BrCl and Br_2 in roughly equal amounts. They determined an uptake coefficient for the process of $\approx 1 - 3 \times 10^{-3}$. As detailed in Sect. 2, the present work has clearly shown that the use of HOBr concentrations in excess of 10^{11} cm^{-3} in studies of the HOBr uptake to salt surfaces can strongly influence both the kinetic behaviour and the ratio of the Br_2 and BrCl products, and can also lead to the formation of Br_2O on the surface. The factor of 10 difference in the uptake coefficient and the vastly different product distribution seen by these authors can therefore be explained by their use of $\approx 10^{13}$ cm^{-3} HOBr, i.e. a factor of 1000 greater than routinely used in the present study. As we have already shown, the use of high concentrations of HOBr leads to rapid depletion of surface bromide, and increases the ratio of BrCl to Br_2 observed in the gas-phase. At the same time, at such high HOBr concentrations, we expect a very rapid surface saturation that leads to a much lower uptake coefficient after an initially high value. Even at concentrations of $\approx 10^{11}$ cm^{-3} this effect is apparent, and at 10^{13} cm^{-3} the initial high uptake coefficient, would not be observable. Following the initial large uptake, the subsequent low uptake is also expected to show some time dependence, and results in curvature in plots of HOBr signal versus injector position. Indeed, a close examination of the raw data presented by Kirchner et al. (1997) reveals pronounced curvature in several of the uptake profiles. The low uptake coefficient measured by these authors probably corresponds to uptake onto a surface that is severely depleted in available reactive sites.

There have been several studies of the uptake of HOBr onto pure ice surfaces, which reveal a number of common features (Abbatt, 1994; Allanic et al., 1997; Chu and Chu, 1999; Chaix et al., 2000) including a strong negative temperature dependence of the uptake coefficient between 175 and 239 K, and the formation of Br_2 and BrCl products when the surface is doped with HBr or HCl respectively. The uptake coefficients measured in these studies vary from $\gamma \approx 0.5$ at 175 K to $\gamma \approx 10^{-3}$ at ≈ 230 K on pure ice. The uptake coefficients on pure ice at 230 K are thus lower that those measured on the frozen salt substrates of the present study, which were $\gamma \approx 10^{-2}$ at 230 K. On the other hand, the presence of HCl on the surface increases the uptake coefficient up to $\gamma \approx 0.2$ at temperature close to 230 K, depending on the amount of HCl available on the surface for reaction (Abbatt, 1994; Chu and Chu, 1999). The observed formation of BrCl and Br_2 when Cl^- and Br^- are available at the surface
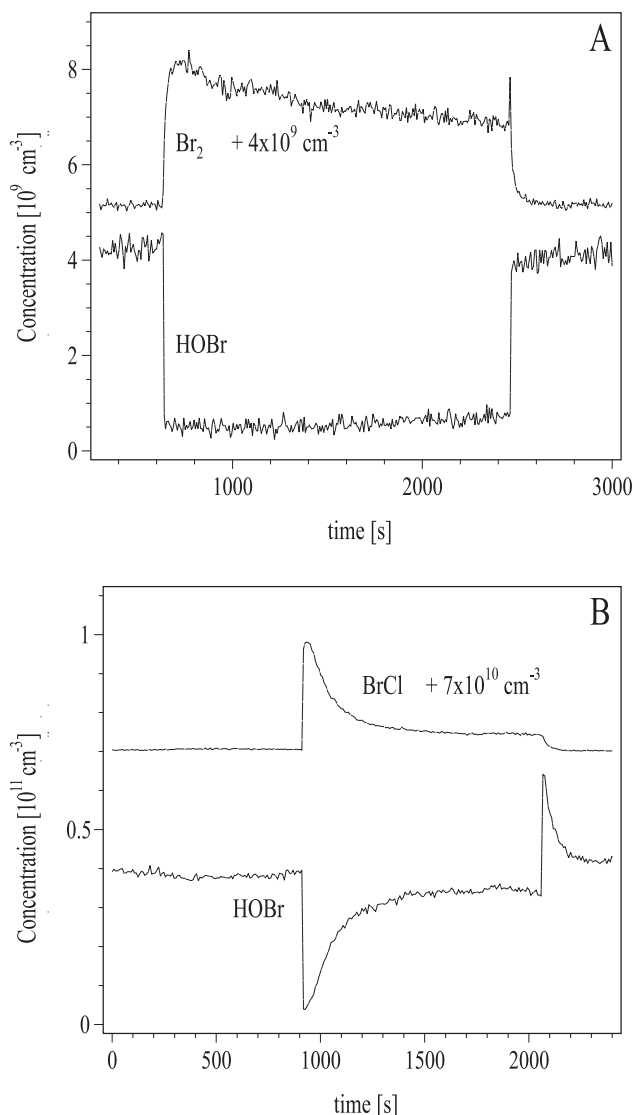

Fig. 8. Uptake of HOBr onto dried salt surface at 233 K **(a)** 2 M NaCl, 3×10^{-3} M NaBr, **(b)** 2 M NaCl, 0 M NaBr.

is compatible with the present results, as is the observation of a fast reaction of BrCl with surface adsorbed HBr on ice surfaces at $180 - 210$ K to form Br_2 (Allanic et al., 2000).

The interaction of HOBr with dry NaCl and KBr surfaces has been examined at room temperature (Mochida et al., 1998). In that study no data were obtained for mixed salt surfaces. For reaction with NaCl, the products observed were BrCl and Br_2, whereby the Br_2 was believed to arise from a self-reaction of HOBr on the surface, and decomposition of the subsequently formed Br_2O. The BrCl evolution into the gas-phase displayed an induction period as observed in the present work. Br_2 was observed as the sole gas-phase product of the HOBr + KBr interaction. Mochida et al. (1998) reported initial uptake coefficients of $\gamma = (6.5 \pm 2.5) \times 10^{-3}$ for NaCl and $\gamma = (0.18 \pm 0.04)$ for KBr.

3.7.2 BrCl, Cl$_2$ and Br$_2$ uptake to frozen and dry surfaces

There have been a number of studies of the interactions of the di-halogens BrCl, Cl$_2$ and Br$_2$ with both dry and frozen salt surfaces. Berko et al. (1991) examined qualitative aspects of the uptake and reaction of Cl$_2$ and BrCl with dry NaBr crystals. They found that whilst BrCl reacted with NaBr to form Br$_2$ directly, the uptake of Cl$_2$ resulted in initial formation and release of Br$_2$, followed by BrCl. This is consistent with the present results and mechanism for reaction of Cl$_2$ with mixed salt surfaces. BrCl is formed in the first step of the reaction in which Cl$_2$ reacts with NaBr, but is converted to Br$_2$ before it can leave the bromide-rich surface. Only after the surface has been sufficiently depleted in Br$^-$ can BrCl escape to the gas-phase. Kinetic data on the reaction of Cl$_2$ with dry synthetic sea-salt have also been obtained, and an uptake coefficient of $\gamma \approx 2 \times 10^{-2}$ reported (Mochida et al., 1998). As in the present study, Br$_2$ (rather than BrCl) was observed as the dominant product. The reaction of Cl$_2$ with frozen, mixed salt surfaces of similar composition to those reported here was examined by Huff and Abbatt (2000). They found an efficient interaction at 248 K, but no evidence for reaction at 233 K ($\gamma < 0.002$), which the authors reported as surprising. This observation contrasts the present result in which the uptake coefficient was found to be greater than 0.028 at 233 K, and where Br$_2$ product was observed at high yield. The result of Huff and Abbatt (2000) at 248 K, whereby an uptake coefficient of $\gamma = 0.048$ was obtained is more in line with the present observations, as is the observation that Br$_2$ is the dominant product (98–99%). These authors also carried out a detailed study of the reaction of Cl$_2$ with surfaces prepared from solutions containing various amounts of Br$^-$ (in the absence of Cl$^-$) and found a strong dependence of the uptake coefficient on this parameter at 233 K.

The same authors have also examined the reaction of BrCl with frozen, Br$^-$ containing salt surfaces and also find an efficient conversion of BrCl to Br$_2$ and an uptake coefficient that depended on the Br$^-$ concentration, with values of $\gamma = 0.018$ for [Br$^-$] = 0.01 M, and $\gamma = 0.042$ for [Br$^-$] = 0.1 M. Importantly, for reaction of both Cl$_2$ and BrCl, they also observed no dependence of the uptake coefficient on the pH of the solution used to prepare the surface, which is consistent with the present observations for HOBr.

4 Conclusions and implications for the chemistry of the polar boundary layer

In the present study it has been shown that HOBr reacts efficiently with surfaces prepared by freezing synthetic salt solutions of similar Br$^-$ / Cl$^-$ ratio and ionic strength to sea water. Use of very low HOBr concentrations has enabled us to show that previous results (Kirchner et al., 1997) on both the uptake coefficient and product yields were erroneous due to use of very high HOBr concentrations in the gas-phase, that modified the relative surface abundance of Br$^-$ and Cl$^-$ on the time scale of the measurements. Various aspects of our observations are discussed below in the context of their implications for helping us understand the cause of low ozone events (LOEs) in both the Arctic and Antarctic boundary layers. In doing this we note that whereas our laboratory-made surfaces, prepared from pure chloride / bromide solutions are not perfect replicas of sea-ice, or sea-spray that has been deposited on the ice pack, they allow the variation of parameters (i.e. the Cl$^-$ to Br$^-$ ratio and the pH) that enable us to gain some insight into the chemical mechanisms of halogen activation and release.

Firstly we note that the uptake of HOBr to a fresh, frozen sea-salt surface does not initially lead to the release of BrCl, which is consistent with our measurements in the aqueous phase (Fickert et al., 1999). A significant depletion of surface Br$^-$ is necessary before the slow rate of desorption of BrCl from the surface allows it to compete with its transformation to Br$_2$. If halogen activation is initiated by gas-phase bromine chemistry that leads to HOBr formation, we would predict first bromine activation and later the release of chlorine. At first glance, this appears to disagree with the results of Ramacher et al. (1999) who, by making measurements of hydrocarbon depletion rates, were able to show that during each ozone depletion event the time integrated chlorine atom concentration increases earlier than the bromine. However, as discussed by these authors, the presence of high concentrations of Br atoms (available to react with hydrocarbons) is precluded by ozone mixing ratios in excess of ≈ 10 ppb, whereas Cl atom / hydrocarbon reactions are relatively unaffected by the presence of these ozone concentrations.

We also observe that, in stark contrast to reaction in the aqueous phase, the uptake of HOBr to Br$^-$ / Cl$^-$ containing ice surfaces leads to release of molecular di-halogens at high yield even at low H$^+$ concentrations. In the marine boundary layer at mid-latitudes the deposition of HOBr to the surface of the sea does not lead to release of di-halogens, but requires the acidification of aerosol sea-spray by uptake of gases such as SO$_2$, HNO$_3$ (Sander and Crutzen, 1996) or methane sulphonic acid (Ayers et al., 1999) (MSA), and gives halogen activation a strong dependence on the concentration of airborne particles, and thus wind strength. In very clean environments, and in the absence of a significant source of CH$_3$SCH$_3$ (precursor of MSA), di-halogen activation by HOBr uptake is therefore inoperative. Our observation that the uptake of HOBr and the formation of Br$_2$ or BrCl is efficient on dry and frozen salt surfaces made from non-acidified solutions may help explain why low ozone events still occur in the clean air of the Antarctic even though mechanisms to acidify particles may not be available. A complicating issue here is caused by the presence of a liquid-phase which is believed to be associated with these frozen surfaces, and in which high concentrations of Cl$^-$ and Br$^-$ are expected to be present (Koop et al., 2000). The reaction of HOBr

Table 2. Summary of kinetic and product data obtained for uptake of BrCl, Cl_2 and Br_2 onto frozen salt surfaces, and HOBr onto dry (and humidified)[1] salt surfaces
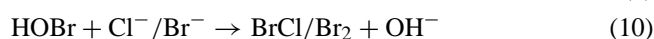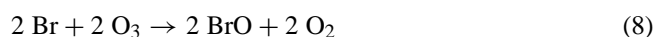
Trace gas	Surface[2]	T K	Major Products[3]	γ_{init}
BrCl	Br^- / Cl^- (Frozen)	233	Br_2	> 0.034
Br_2	Br^- / Cl^- (Frozen)	233	Br_2	> 0.025
Br_2	Br^- (Frozen)	243	Br_2	> 0.01
Cl_2	Br^- / Cl^- (Frozen)	233	Br_2	> 0.028
HOBr	Br^- / Cl^- (Dry)	243	Br_2	0.02
HOBr	Cl^- (Dry)	233	BrCl	0.06

[1]Relative humidity varied from 0 to 100%.
[2]Br^-/Cl^- surfaces were made from 2 M Cl^- / 3×10^{-3} M Br^- solutions. The Cl^- surfaces were prepared from 2 M Cl^- solutions, the Br^- surfaces were prepared from 3×10^{-3} M solutions.
[3]Product formed at short exposure times. The evolution of the product distribution as a function of reaction time is described in the text.

with Cl^- and or Br^- in liquid environments should require a pH which is lower than that of sea-water to result in halogen activation as long as sufficient liquid is present to cause dissolution and ionisation of HOBr. Our measurements of the uptake coefficient of HOBr on frozen sea-salt surfaces of $\gamma = 2 \times 10^{-2}$ enables comparison between, and linking of the heterogeneous and homogeneous gas-phase processes occurring in the boundary layer at the poles during a LOE to be made. If most of the heterogeneous chemistry involving salt surfaces is taking place at the snow pack rather than in suspended sea-salt aerosols (Tang and McConnell, 1996; Sander et al., 1997), values of γ of this magnitude imply that the rate of reaction of HOBr at the surface of the snow pack will be limited by its deposition velocity, which, following Huff and Abbatt (2000), and assuming a mixed layer of 100 m height, is ≈ 0.6 cm s^{-1}. Although there may be a weak source of Br atoms due to the photolysis of bromoform (Barrie et al., 1988), which may be sufficient to initiate bromine chemistry at polar sunrise, most photochemical activity will take place close to the snow pack, where Br_2 is released and photolysed (to form two Br atoms, Reaction 8) on time scales that may be short relative to times required for vertical mixing. The Br atoms can react with O_3 to form BrO.

$$Br_2 + h\nu \rightarrow 2\,Br \tag{7}$$

$$2\,Br + 2\,O_3 \rightarrow 2\,BrO + 2\,O_2 \tag{8}$$

$$BrO + HO_2 \rightarrow HOBr + O_2 \tag{9}$$

$$HOBr + Cl^-/Br^- \rightarrow BrCl/Br_2 + OH^- \tag{10}$$

At normal levels of O_3 (≈ 40 ppb, Hausmann and Platt, 1994; Hopper et al., 1998), most Br atoms will react with O_3, and the loss of one HOBr in a heterogeneous process and the formation of 2 HOBr via Reaction sequence (8 and 9) implies that the photochemical / heterogeneous chemistry taking place at the snow pack is of a chain branching nature,

and will result in efficient release of reactive halogen species as long as sufficient Br^- is present in the surface snow-pack and sufficient O_3 is present in the gas-phase so that formation of BrO is efficient compared to reaction with aldehydes. If the reservoir of Br^- is significantly depleted before all gas-phase O_3 has been consumed, then chlorine activation can be expected, as BrCl is released in preference to Br_2. Fast surface reactions and the short lifetimes of the reactive bromine species with respect to photo-dissociation imply that mixing of O_3 rich air masses distant from the snow pack with O_3 poor air masses very close to the surface will be important in determining the occurrence and duration of LOEs. These considerations preclude a simple description of the heterogeneous and gas-phase reactions that initiate and maintain high concentrations of reactive halogens in the polar boundary layer, which can only be done with the use of models that contain both gas-phase and heterogeneous halogen chemistry (the objectives of this paper) and appropriate parameterisation of mixing and transport of air masses over the snow pack. The reader is referred to the recent modelling study by Michalowski et al. (2000) which shows that O_3 depletion is very sensitive to the concentration of HOBr, and the rate of its uptake to Br^- and Cl^- containing surfaces.

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