Release of gas-phase halogens from sodium halide substrates: heterogeneous oxidation of frozen solutions and desiccated salts by hydroxyl radicals

S J Sjostedt and J P D Abbatt

Department of Chemistry, University of Toronto, 80 St George Street, Toronto, ON M5S 3H6, Canada

Received 3 June 2008
Accepted for publication 19 September 2008
Published 19 November 2008
Online at stacks.iop.org/ERL/3/045007

Abstract
Motivated by the need to determine the mechanism of the initial release of halogens from sea ice and marine aerosol substrates, a study of the interactions of OH radicals with a variety of halide-containing surfaces has been performed in a coated-wall flow tube using chemical ionization mass spectrometry for gas-phase analysis. The salts studied were NaCl with 0.01% and 0.002% impurities of Br\(^-\) and I\(^-\) respectively, and NaCl/NaBr mixtures with Cl\(^-\)/Br\(^-\) seawater ratios. The surfaces were desiccated salts, desiccated salts exposed to elevated relative humidity, and frozen solutions. In all cases, gas-phase Br\(_2\) and BrCl were formed, with the Br\(_2\) yield (defined as a molar ratio of halogen produced to OH lost) larger than 0.2 and the BrCl yield as roughly 0.01. For the first time, an observation of heterogeneous release of iodine-containing halogens (in particular IBr) was made with yields comparable to those of BrCl. We note that pH neutral frozen solutions demonstrated halogen release, although the yields were higher for acidic frozen solutions.

Keywords: halogens, hydroxyl radical, heterogeneous chemistry

1. Introduction

It is well established that halogen chemistry plays a significant role in selected tropospheric environments (e.g. Platt and Honninger 2003, von Glasow et al 2004). Arctic ozone depletion events with concomitant increases of BrO (Barrie et al 1988) have been observed consistently over the past two decades. Subsequent field campaigns have further investigated the role of halogens at high latitudes (Hausmann and Platt 1994, Foster et al 2001, Avalone et al 2003) and other environments such as dry lake beds (Hebestreit et al 1999, Stutz et al 1999) and the marine boundary layer (Saiz-Lopez et al 2006, Bloss et al 2005).

Gas-phase chemistry has proven incapable of explaining the observed extended ozone depletion events. Therefore, heterogeneous reaction mechanisms, such as the autocatalytic bromine explosion (Vogt et al 1996), have been invoked to provide an additional halogen source. In the marine boundary layer aged aerosols have displayed depleted bromine to sodium ratios with respect to seawater (Sander et al 2003). This suggests that bromine has been preferentially removed from the aerosol over its lifetime. The release of halogens from dry salts (Finlayson-Pitts 2003, Rossi 2003) has also been investigated in laboratory studies.

Despite these studies, the mechanisms that release halogens to initiate these cycles remain ill-defined, which limits our predictive capabilities. There are a number of possibilities, including a dark reaction involving O\(_3\) (Oum et al 1998b), interactions with NO\(_x\) (Finlayson-Pitts et al 1990), and free radical processes (Mozurkewich 1995, Matthew et al 2003). In this regard, Frinak and Abbatt (2006) investigated halogen release from NaCl/NaBr solutions by heterogeneous
oxidation involving hydroxyl radicals (OH). Both Br$_2$ and Cl$_2$ were released from acidic solutions. In this letter, we extend this work by examining the release of halogens by OH interactions with desiccated salts and frozen sodium halide solutions. Of interest is whether the relationship between acidity and halogen release is maintained on ice surfaces and whether halogen release occurs from neutral substrates, as described by Finlayson-Pitts (2003). To our knowledge, this is the first investigation of the interactions of OH with halide surfaces of this type.

2. Experimental details

Observations of gas-phase halogens were obtained with a chemical ionization mass spectrometer (CIMS) coupled to a coated-wall flow tube. This apparatus allows for controlled exposure of hydroxyl radicals to prepared surfaces, as described in Frinak and Abbatt (2006). Briefly, the operating pressure of the flow tube was 90 Torr with a total flow rate of 1.5 lpm of N$_2$. Water vapor mixing ratios were controlled by passing a fraction of the carrier gas through a bubbler before entering the flow tube. Within the CIMS ionization region, a trace flow of SF$_6$ in 10.5 lpm of dry N$_2$ passed over a 210Po ion source. SF$_6$ was chosen as the reagent ion (Huey et al 1995, Bertram et al 2001) because it allowed for simultaneous detection of NO$_2$ as well as multiple halogen-containing species (Br$_2$, BrCl, IBr, HCl, and Cl$_2$).

A 3 ml aliquot of sodium halide solution was added to a 1.5 cm i.d., 30 cm-long rotatable glass insert that had been washed first with a 5% HF solution and then with lots of 18 MΩ water. For preparation of desiccated salts, the solution was gradually dried for a period of roughly two hours while rotating the tube under vacuum. This will have prepared surfaces that will not have liquid water present but will have significant amounts of strongly adsorbed water. In particular, the pressure within the flow tube was gradually lowered from ambient to 90 Torr with a low flow (<1 lpm) of dry N$_2$ passing over the substrate. For frozen solutions, the aliquot was lowered to a temperature of 248 K, with a humidified flow (<1 lpm) of dry N$_2$ passing over the substrate. Once frozen, the pressure of the flow tube was lowered to 90 Torr. Solutions used were 3.4 M NaCl (ACP 0.01% Br$^-$, 0.002% I$^-$ impurities by mass) i.e. [Cl$^-$/[Br$^-$] = 13 700:1; [Cl$^-$/[I$^-$] = 109 000:1 and 3.4 M NaCl/0.005 M NaBr i.e. [Cl$^-$/[Br$^-$] = 680:1, which we refer to as NaCl and sea-salt respectively. H$_2$SO$_4$ was used to acidify the solutions. Solutions that we refer to as pH neutral had a pH of 6.5–7.0.

When the desired substrate phase had been obtained, a 100 sccm flow of Ar-containing trace H$_2$ was flowed through a microwave generated plasma. The resulting hydrogen atoms were then introduced into a controlled flow of a known quantity of NO$_2$ gas to generate OH, within a glass injector positioned with its tip at the upstream end of the coated glass insert.

\[
H + NO_2 \rightarrow OH + NO. \tag{1}
\]

The initial OH concentrations used in the experiments are high with a median number density of $5 \times 10^{11}$ molecules cm$^{-3}$. As described in Frinak and Abbatt (2006), these concentrations were determined by assuming that all of the NO$_2$ loss was due to formation of OH and we consider them to have an absolute uncertainty of roughly a factor of two.

As determined by calibrations using known flows from gas bulb standards, the limits of detection were $6 \times 10^9$ and $5 \times 10^8$ molecules cm$^{-3}$ for NO$_2$ and Br$_2$ respectively, of a 30 s integration period where $S/N = 1$. Their sensitivities were $3.1 \times 10^{-16}$ Hz/molecules/cm$^3$ for NO$_2$ and $2.4 \times 10^{-19}$ Hz/molecules/cm$^3$ for Br$_2$. The detection limits are considerably enhanced over Frinak and Abbatt (2006) and we believe this is due in part to lessened interference from water vapor. The sensitivities of BrCl and IBr were assumed to be the same as Br$_2$.

3. Results

The effects of phase, acidity and bromide concentration of the bulk substrate on the release of halogen gases were investigated. In particular, experiments were run over frozen solutions (248 K), desiccated salts (298 and 253 K) and humidified salts (258 and 253 K). For the humidified salt experiments, the relative humidity in the flow tube was set between the deliquescence relative humidities for NaBr (58%) and NaCl (75%) so that thermodynamics would predict that most of the NaCl will have been in the solid state and the NaBr in solution (Koop et al 2000). However, we note that we have no evidence ruling out the possibility that the surfaces had additional liquid character arising from metastable solutions.

To best quantify the release of halogens relative to OH exposure, experiments were frequently conducted as a series of runs, where a run is a 15 min period where the OH source was turned on. The amount of halogen release was then calculated from the change in signal on and signal off (see figure 1, for an example). Initially, Br$_2$ and Cl$_2$ were the two halogen species observed. In particular, Frinak and Abbatt (2006) observed an initial release of Br$_2$ and then later a Cl$_2$ release from liquid substrates. Here, Cl$_2$ was not observed even after prolonged (i.e. multiple hour) exposure to OH, even though the experimental configuration is the same as that of Frinak and Abbatt (2006) and so should have been observed if formed in reasonable yields. However, small signals of other species such as BrCl and IBr were observed, in addition to a large signal from Br$_2$. Initially the signals rose slowly with exposure, presumably as the downstream salt surfaces became conditioned with the halogens, and then a steady signal was observed. For each run, the OH concentration was determined by the change in NO$_2$ signal from when the microwave signal was off and on. As demonstrated in Frinak and Abbatt (2006), all OH radicals were lost via interactions with the coated walls of the glass insert, and there is minimal gas-phase loss.

The results of the OH initiated release of gas-phase halogen species are summarized in table 1, which shows the maximum ratio of gas-phase halogen release to OH loss for each substrate and the run at which the maximum was observed. Typically 1 to 2 experiments were conducted for each set of conditions. When multiple experiments of the same substrate were performed, the mean ratios and range of values are presented. Note that IBr was not monitored in the runs with NaCl.
Figure 1. A time series from an experiment with a frozen acidified sea-salt solution at 248 K. The left axis is for the Br₂ and NO₂ signals, the right axis is for the BrCl and IBr signals.

Table 1. Halogen product yields for exposure to OH to different substrates.

| Substrate                | Run | [Br₂]/[OH] | Run | [BrCl]/[OH] | Run | [IBr]/[OH] |
|--------------------------|-----|------------|-----|------------|-----|------------|
| Desiccated salt (NaCl)   | 1   | 0.6        | 6   | 0.008      | NA  |            |
| Desiccated salt (sea-salt)| 1   | 0.4        | 4   | 0.010      | 1   | 0.005      |
| Humidified salt (NaCl)   | 2   | 0.22 ± 0.06| 7   | 0.018 ± 0.004| NA |            |
| Humidified salt (sea-salt)| 5   | 0.40 ± 0.14| 7   | 0.010 ± 0.001| 4   | 0.016 ± 0.011|
| Frozen solution pH = 7 (NaCl)| 1   | 0.28 ± 0.10| 3   | 0.019 ± 0.003| NA |            |
| Frozen solution pH = 7 (sea-salt)| 3   | 0.22 ± 0.01| 6   | 0.007 ± 0.002| 2   | 0.007 ± 0.002|
| Frozen solution pH = 2 (sea-salt)| 7   | 1.20 ± 0.14| 8   | 0.020      | 5   | 0.030 ± 0.003|

a ‘Run’ refers to the run number at which the maximum ratio was observed.

The effect of pH was initially to be investigated for both desiccated salts and frozen solutions. However, after the acidified bulk solution was dried the CIMS spectrum was dominated by gas-phase HCl. Several hours of dry N₂ were required to bring the HCl concentrations down to a level where SF₆ was again the dominant ion. Given the significant gas-phase concentrations present, and because the surfaces may have been significantly modified from the high level of HCl release, no experiments were conducted with these substrates. However, the effect of pH could be investigated for the frozen sea-salt solutions where this enhanced gas-phase HCl was not observed. Presumably the HCl was sufficiently soluble in the substrate that it was not easily volatilized.

Figure 2 shows that the release of Br₂ from an acidified surface was a factor of five greater than from a neutral surface. In this figure, the signals have been normalized to a constant OH concentration to enable a meaningful comparison of product yields from one experiment to another. Acidification of the frozen sea-salt substrate sustains the release of Br₂ over the entire experiment, whereas the neutral frozen sea-salt substrate achieves an early maximum and then gradually decreases over the remainder of the experiment. The release of IBr and BrCl are also enhanced at lower pH and the release of BrCl occurs later than either IBr or Br₂.

In figure 3 the effect of Br⁻ concentration on halogen release from frozen pH neutral solutions is explored for NaCl and sea-salt substrates. As noted in section 2, although the [Cl⁻]/[Br⁻] = 13 700:1 for NaCl, Br₂ is the dominant gas observed. The release of BrCl was also observed but there was no evidence of gas-phase Cl₂. For both NaCl and sea-salt substrates, the observed maximum signal of gas-phase BrCl occurs after the maximum of Br₂ indicating that BrCl formation occurs once the Br⁻ ion concentration has been depleted. The sustained production of Br₂ from the sea-salt and the higher yield of BrCl from the NaCl also reinforce this conclusion.

In figure 4, experiments were conducted with neutral sea-salt substrates where the plasma was left on for ~2.5 h to investigate how prolonged exposure to OH would affect the release of Br₂ from different phases. The release of Br₂ is dominated by an initial burst that rapidly drops off. At experiment end the release of Br₂ is an order of magnitude lower than initially. In contrast, the release of Br₂ from the frozen solution remains fairly constant throughout albeit roughly a factor of three lower than the maximum observed for
Figure 2. Comparison of halogen release as a function of bulk substrate pH for frozen sea-salt solutions at 248 K. Signals have been normalized to the amount of OH. Note that each run refers to a 15 min period during which there was OH exposure.

Figure 3. The release of Br\(_2\) and BrCl from pH neutral frozen solutions as function of bromide concentration at 248 K. Signals have been normalized to the amount of OH. Note that each run refers to a 15 min period during which there was OH exposure.

4. Discussion

To summarize the findings from the results we note that (i) Br\(_2\) is the primary halogen product for OH heterogeneous interactions with the surfaces, with smaller yields of BrCl but no observations of Cl\(_2\), even with prolonged exposure; (ii) frozen acidified solutions yield more halogens than neutral substrates; (iii) enhanced concentrations of Br\(^-\) lead to more sustained release of Br\(_2\) and delayed BrCl release; (iv) frozen solutions lead to more sustained release than solid salts; and (v) an iodine-containing product (IBr) is observed. To discuss these findings, potential reaction mechanisms will be presented.

In an earlier study by Frinak and Abbatt (2006), it was established that aqueous solutions also exhibit halogen release upon exposure to gas-phase OH, and that enhanced yields are observed from more acidic substrates. In that work, the CIMS sensitivity was not nearly as high as in this study so the lack of halogen products observed under neutral conditions (and the lack of observation of BrCl and IBr) may have arisen from their concentrations being below detection limits. This work indicates that halogens can indeed be released from neutral solid substrates. To determine that there were no experimental artifacts in this regard and noting that the pH of solutions may change upon freezing (Robinson et al. 2006) we tested this observation by one set of experiments on frozen solutions formed from pH 9 solution and still observed halogen release.

We focus initially on pathways to form the principal product, Br\(_2\), and to explain the acidity enhancement (for more details on the mechanism and rate constants of specific...
Figure 4. Comparison of gas-phase Br\textsubscript{2} release from pH neutral sea-salt as a function of substrate phase at 248–253 K. The solid line represents ice, the dashed line represents desiccated salt and the dotted line represents a humidified salt. The signals have been normalized to the amount of OH.

reactions see Finlayson-Pitts (2003), or Frinak and Abbatt (2006)). In particular, although interfacial chemistry is likely to dominate, it is not known whether OH will initially react with a Br\textsuperscript{−} ion on the surface or a Cl\textsuperscript{−} ion. Given that the bulk concentration of Cl\textsuperscript{−} dwarfs that of Br\textsuperscript{−}, it is possible that the initial interaction is with Cl\textsuperscript{−}:

$$\text{OH} + \text{Cl}^{-} \leftrightarrow \text{HOCl}^{-} \quad \text{(2)}$$

$$\text{HOCl}^{-} + \text{H}^{+} \rightarrow \text{Cl}^{-} + \text{H}_{2}\text{O} \quad \text{(3)}$$

$$\text{Cl}^{-} + \text{Cl}^{-} \rightarrow \text{Cl}_{2}^{-} \quad \text{(4)}$$

$$\text{Cl}_{2}^{-} + \text{Br}^{-} \rightarrow \text{BrCl}^{-} + \text{Cl}^{-} \quad \text{(5)}$$

$$\text{BrCl}^{-} + \text{Br}^{-} \rightarrow \text{Br}^{-} + \text{Cl}^{-} \quad \text{(6)}$$

$$\text{Br}_{2}^{-} + \text{Br}_{2}^{-} \leftrightarrow \text{Br}_{3}^{-} + \text{Br}^{-} \quad \text{(7)}$$

$$\text{Br}_{3}^{-} \leftrightarrow \text{Br}_{2}^{2-} + \text{Br}^{-} \quad \text{(8)}$$

Note that the acidity dependence appears in the competition between reactions (3) and (4), relative to the loss rate back to form OH. Also, if the Br\textsuperscript{−} concentration drops, then we postulate that BrCl could form via self-reaction of BrCl\textsuperscript{−}:

$$\text{OHBr}^{-} + \text{H}^{+} \rightarrow \text{Br} + \text{H}_{2}\text{O} \quad \text{(11)}$$

$$\text{HOBr}^{-} + \text{Br}^{-} \rightarrow \text{Br}_{2}^{-} + \text{OH}^{-} \quad \text{(12)}$$

$$\text{Br} + \text{Br}^{-} \leftrightarrow \text{Br}_{2}^{-} \quad \text{(13)}$$

followed by reactions (8) and (9) to form Br\textsubscript{2}. Again, an acidity dependence would arise via the competition between reactions (11) and (12).

Finally, there is also the possibility of a surface reaction mechanism involving the self-reaction of short-lived OH–halide complexes but not involving protons (Oum et al 1998a, Finlayson-Pitts 2003):

$$\text{OH} + \text{Cl}^{-} \rightarrow \text{OHCl}^{-} \quad \text{(14)}$$

$$\text{OH} + \text{Br}^{-} \rightarrow \text{OHBr}^{-} \quad \text{(15)}$$

$$\text{OHBr}^{-} + \text{OHBr}^{-} \rightarrow \text{Br}_{2} + 2\text{OH}^{-} \quad \text{(16)}$$

$$\text{OHCl}^{-} + \text{OHBr}^{-} \rightarrow \text{BrCl} + 2\text{OH}^{-} \quad \text{(17)}$$

Molecular dynamics studies by Roeselova et al (2003) infer that the length of time that OH is adsorbed to a surface is sufficient for heterogeneous chemistry of this type to occur in the interfacial region.

For aqueous-phase substrates, Frinak and Abbatt (2006) observed the release of Cl\textsubscript{2} as the signal due to Br\textsubscript{2} dropped, presumably due to Br\textsuperscript{−} depletion. In this work, we did not see the release of Cl\textsubscript{2} from any of the substrates even after running experiments for as long as 12 h. Two effects might explain this. First, the phase was different in these experiments, with the vast majority of the chloride in the solid phase as either NaCl or NaCl\textsubscript{·}2H\textsubscript{2}O. Thus, chloride would not be as available for reaction. Also, there would be a significant enhancement of Br\textsuperscript{−} at the top of the substrate, arising from the manner of substrate preparation. In particular, exclusion of ions during solution freezing may form a highly concentrated halide layer at the surface. Depletion of this layer of Br\textsuperscript{−} may not occur as readily as it does in the uppermost layers of a solution that does not experience the same degree of concentration enhancement.
We note that we observe the release of IBr from the frozen solutions, even though iodide is present at only the 0.002% level in the NaCl salt. This is consistent with iodine being more easily oxidized than other halides, and with it also being more surface active (Ghosal et al 2005).

Finally, the phase of the substrate had an effect on the temporal profile of the halogen release. For the desiccated salt, although there may be a few layers of surface-adsorbed water, it is expected that both the bromide and chloride will be predominantly in the solid phase. Br₂ release was prompt from these surfaces, followed by a rapid decline in signal. This is consistent with there being depletion of surficial bromide and protons that are not readily replenished due to slow diffusion times from the bulk. In the case of the mechanism initiated by reactions (14) or (15), the formation of NaOH may poison the surface.

For frozen solutions, we note that there will be small pockets of bromide-containing brine given that the eutectic surface is intermediate between the desiccated salts and humidified salts is the surface. For frozen solutions, we note that there will be small pockets of bromide-containing brine given that the eutectic surface is intermediate between the desiccated salts and humidified salts is intermediate between the desiccated salts and frozen solutions probably because the humidity was high enough to deliquesce the sodium bromide.

5. Conclusions

All the pH neutral substrates display the release of gas-phase halogens, primarily Br₂, upon exposure to gas-phase OH. The release was initially most pronounced with the desiccated salts due to the high concentration of Br⁻ ions at the surface. For frozen solution substrates and humidified salts, the product release was more sustained with time, indicative of replenishment of halide ions at the surface. An acidity dependence was observed for the halogen release from the ice substrate, with the yields of all the halogens increasing when acidic solutions were used. Lastly, an oxidized iodine product, IBr, was observed. From an environmental perspective, this work demonstrates that these surfaces, whether neutral or acidified, are fully able to act as sources of atmospheric halogens, principally Br₂, when exposed to gas-phase OH.

Acknowledgments

The authors acknowledge E Frinak in experimental design and NSERC for funding.

References

Avallone L M, Toohey D T, Fortin T J, McKinney K A and Fuentes J D 2003 In situ measurements of bromine oxide at two high-latitude boundary layer sites: implications of variability J. Geophys. Res. 108 4089
Barrie L A, Bottineau J W, Schnell R C, Crutzen P J and Rasmussen R A 1988 Ozone destruction and photochemical reactions at polar sunrise in the lower Arctic troposphere Nature 334 138–41
Bertram A K, Ivanov A V, Hunter M, Molina L T and Molina M J 2001 The reaction probability of OH on organic species of tropospheric interest J. Phys. Chem. A 105 9415–21
Bloss W J et al 2005 Impact of halogen monoxide chemistry upon boundary layer OH and HO₂ concentrations at a coastal site Geophys. Res. Lett. 32 L08814
Finlayson-Pitts B J 2003 The tropospheric chemistry of sea-salt: a molecular-level view of the chemistry of NaCl and NaBr Chem. Rev. 103 4801–22
Finlayson-Pitts B J, Livingston F E and Berko H N 1990 Ozone destruction and bromine photochemistry at ground-level in the Arctic spring Nature 343 622–5
Foster K L, PlaBtridge R A, Bottenheim J W, Shepson P B, Finlayson-Pitts B J and Spicer C W 2001 The role of Br₂ and BrCl in surface ozone destruction at polar sunrise Science 291 471–4
Frinak E K and Abbatt J P D 2006 Br₂ production from the heterogeneous reaction of gas-phase OH with aqueous salt solutions: impacts of acidity, halide concentration, and organic surfactants J. Phys. Chem. A 110 10456–64
Ghosal S, Hemminger J C, Bluhm H, Mun B S, Hebenstreit L D, Ketteler G, Ogletree D F, Requejo F G and Salmeron M 2005 Electron spectroscopy of aqueous solution interfaces reveals surface enrichment of halides Science 307 563–6
Hausmann M and Platt U 1994 Spectroscopic measurement of bromine oxide and ozone in the high Arctic during the polar summer experiment 1992 J. Geophys. Res. 99 25399–41
Hebestreit K, Stutz J, Rosen D, Matveiv V, Peleg M, Luria M and Platt U 1999 DOAS measurements of tropospheric bromine oxide in mid-latitudes Science 283 55–7
Hess M, Krieger U K, Huthwelker T, Ammann M, Lanford W A and Peter T 2007 Bromine enrichment in the near-surface region of Br-doped NaCl single crystals diagnosed by Rutherford backscattering spectrometry J. Phys. Chem. A 111 4312–21
Huey L G, Hanso D R and Howard J C 1995 Reactions of SF₅⁻ and I⁻ with atmospheric trace gases J. Phys. Chem. 99 5001–8
Jungwirth P and Tobias D J 2006 Specific ion effects at the air/aqueous interface Chem. Rev. 106 1259–81
Koop T, Kaplunashvili A, Molina L T and Molina M J 2000 Phase transitions of sea-salt/water mixtures at low temperatures: implications for ozone chemistry in the polar marine boundary layer J. Geophys. Res. 105 26393–402
Matthew B M, George I and Anastasio C 2003 Hydroperoxyl radical oxidizes dibromide radical anion to bromide in aqueous solution: implications for the formation of Br₂ in the marine boundary layer Geophys. Res. Lett. 30 2297
Mozurkewich M 1995 Mechanisms for the release of halogens from sea-salt particles by free-radical reactions J. Geophys. Res. 100 14199–207
Oum K W, Lakin M J, DeHaan D O, Brauers T and Finlayson-Pitts-B J 1998a Formation of molecular chlorine from the photolysis of ozone and aqueous sea-salt particles Science 279 74–7
Oum K W, Lakin M J and Finlayson-Pitts-B J 1998b Bromine activation in the troposphere by the dark reaction of O₃ with seawater ice Geophys. Res. Lett. 25 3923–6
Platt U and Honninger G 2003 The role of halogen species in the troposphere Chemosphere 52 325–38
Robinson C, Boxe C S, Guzman M I, Colussi A J and Hoffmann M R 2006 Acidity of frozen electrolyte solutions J. Phys. Chem. B 110 7613–6
Roeselova M, Jungwirth P, Tobias D J and Gerber R B 2003 Impact, trapping, and accommodation of hydroxyl radical and ozone at aqueous salt aerosol surfaces. A molecular dynamics study J. Phys. Chem. B 107 12690–9
Rossi M J 2003 Heterogeneous reactions on salt Chem. Rev. 103 4823–82
Saiz-Lopez A, Shillito J A, Coe H and Plane J M C 2006
Measurements and modeling of I₂, IO, OIO, BrO and NO₃ in
the mid-latitude marine boundary layer Atmos. Chem. Phys.
6 1513–28
Sander R et al 2003 Inorganic bromine in the marine boundary layer:
a critical review Atmos. Chem. Phys. 3 1301–36
Stutz J, Hebestreit K, Alicke B and Platt U 1999 Chemistry of
halogen oxides in the troposphere: comparison of model
calculations with recent field data J. Atmos. Chem. 34 65–85

Vogt R, Crutzen P J and Sander R 1996 A mechanism for halogen
release of sea-salt aerosol in the remote marine boundary layer
Nature 383 327–30
von Glasow R, von Kuhlmann R, Lawrence M G, Platt U and
Crutzen P J 2004 Impact of reactive bromine chemistry in the
troposphere Atmos. Chem. Phys. 4 2481–97
Zangmeister C D, Turner J A and Pemberton J E 2001 Segregation of
NaBr in NaBr/NaCl crystals grown from aqueous solutions:
implications for sea-salt surface chemistry Geophys. Res. Lett.
28 995–8