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Photochemical chlorine and bromine activation from artificial saline snow

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Abstract. The activation of reactive halogen species – particularly Cl_2 – from sea ice and snow surfaces is not well understood. In this study, we used a photochemical snow reactor coupled to a chemical ionization mass spectrometer to investigate the production of Br_2, BrCl and Cl_2 from NaCl/NaBr-doped artificial snow samples. At temperatures above the NaCl-water eutectic, illumination of samples ($\lambda > 310$ nm) in the presence of gas phase O_3 led to the accelerated release of Br_2, BrCl and the release of Cl_2 in a process that was significantly enhanced by acidity, high surface area and additional gas phase Br_2. Cl_2 production was only observed when both light and ozone were present. The total halogen release depended on [ozone] and pre-freezing [NaCl]. Our observations support a "halogen explosion" mechanism occurring within the snowpack, which is initiated by heterogeneous oxidation and propagated by Br_2 or BrCl photolysis and by recycling of HOBr and HOCl into the snowpack. Our study implicates this important role of active chemistry occurring within the interstitial air of aged (i.e. acidic) snow for halogen activation at polar sunrise.

1 Introduction

In the polar regions, heterogeneous reactions occurring on various frozen sea ice surfaces are thought to be responsible for the activation and release of reactive halogen species (particularly Br_2, BrO and HOBr) (Simpson et al., 2007b and references therein). At polar sunrise, reactive bromine species readily dissociate to yield Br radicals that can catalytically destroy ozone or participate in other atmospheric oxidation processes, thereby influencing the oxidative capacity of the polar boundary layer. Although a strong role for bromine in both springtime ozone depletion (Simpson et al., 2007b) and mercury oxidation (Steffen et al., 2008) has now been well established, many of the mechanistic details of bromine activation are still lacking, precluding a good understanding of the environmental conditions and sea ice/snow substrates that lead to such events (Abbatt et al., 2012).

Moreover, the role that *chlorine* plays in these processes is less well known – in part due to a scarcity of reliable field measurements of photolyzable chlorine species (Saiz-Lopez and von Glasow, 2012). Due to the high reactivity of Cl radicals, elevated chlorine levels are also expected to perturb the chemical composition and oxidative capacity of the troposphere, with their greatest impact likely being on the oxidation of volatile organic compounds (Simpson et al., 2007b).

Laboratory studies have shown that oxidation reactions involving O_3 (Oum et al., 1998; Oldridge and Abbatt, 2011; Wren et al., 2010), OH (Sjostedt and Abbatt, 2008) and HOBr (Huff and Abbatt, 2002; Adams et al., 2002; Kirchner et al., 1997) will liberate Br_2 (and in some cases BrCl) but not Cl_2 from frozen halide solutions. Indeed, the dark ozonation of frozen Br^- solutions is thought play an important role in forming "seed" Br_2. The proposed mechanism is based on known aqueous phase chemistry (see Finlayson-Pitts, 2003 and references therein):

$$O_3(g) + Br^- \leftrightarrow OBr^- \tag{R1}$$

$$OBr^- + H^+ \leftrightarrow HOBr \tag{R2}$$

$$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O \tag{R3}$$

When the Br^-/Cl^- is low, HOBr will also oxidize chloride to yield BrCl (Fickert et al., 1999; Adams et al., 2002):

$$HOBr + Cl^- + H^+ \rightarrow BrCl + H_2O \tag{R4}$$
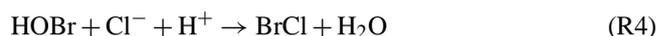
BrCl formed via Reaction (R4) has a lower volatility than Br_2 and may undergo further reactions in the condensed phase to yield $Br_2(g)$ (Finlayson-Pitts, 2003). This, together with the faster rate constant for Reaction (R3) relative to Reaction (R4) (Finlayson-Pitts, 2003), leads to the preferential release of $Br_2(g)$. The analogous dark ozonation of Cl^- Reaction (R5) is too slow to be considered an important Cl_2 source (Finlayson-Pitts, 2003).

$$O_3(g) + Cl^- \leftrightarrow OCl^- \tag{R5}$$

Recent field measurements which have revealed higher-than-expected concentrations of molecular chlorine in the polar boundary layer (up to 400 pptv) (Impey et al., 1997; Stephens et al., 2012; Liao et al., 2013) have therefore left researchers searching for a missing chlorine source. Field measurements by Impey et al. (1997) during the Polar Sunrise Experiment show that Cl_2 follows a diurnal cycle with a daytime maximum, indicating a photochemical source. Recent measurements of Cl_2 at Barrow, AK (USA), suggest that Cl_2 is correlated with both ozone and actinic flux (Liao et al., 2013). These observations motivated the current study, which seeks to investigate whether a reaction involving both light and ozone is responsible for activating chlorine from frozen sea ice/snow surfaces.

The majority of laboratory studies of halogen activation from frozen NaCl/NaBr solutions have been performed using low surface area ice samples; studies performed using high surface area snow samples are completely lacking. Furthermore, motivated by the importance of stratospheric halogen activation, much of the research has been carried out at very low temperatures. There is a need for more studies to be performed at the milder temperatures that are commonly found in the Arctic spring. Not only are such temperatures more relevant for the polar boundary layer, they represent a regime within which sea ice substrates will remain partially liquid and hence the chemistry may be quite different (Koop et al., 2000). Finally, no laboratory studies have been performed in the presence of light, which has the potential to drive HO_x ($= OH + HO_2$) chemistry and halogen radical reactions within the snowpack. Very recently, a field study using natural snow and ice substrates demonstrated the importance of light-driven snowpack chemistry to halogen activation (Pratt et al., 2013). The specific goal of our study was to determine whether a photochemical pathway exists for halogen activation from artificial snow in the presence of gas phase O_3 and radiation at actinic wavelengths. Significant to this study is the choice of high surface area samples and temperatures spanning the NaCl-water eutectic of 252 K. Unlike many previous studies, we chose to focus particularly on chlorine activation by using snow with a low bromide content. In controlled laboratory experiments, we studied the impact of environmental factors such as temperature, acidity, salt content, Br^-/Cl^- ratio, snow surface area and $[O_3]$ on the observed dihalogen release.

Table 1. Parameters used in the experiments. The BASE scenario conditions are shown in bold text.

Parameter	Range
Illumination	310 nm long-pass filter, 360 nm long-pass filter (w/ Xe lamp)
[Ozone]	2.7×10^{13} – $\mathbf{1.3 \times 10^{15}}$ molecules cm^{-3}
Snowpack T	(248, 252, 254, **257**, 263) ± 1 K
Pre-freezing [NaCl]	0.1, **0.5**, 1.0 M
Br^- in NaCl(s)	**< 0.01 wt%** (reagent grade), < 0.001 wt% (high purity)
Pre-freezing pH	**2.3**, 4.3, ambient ($\sim$5.9)
Size fraction	**fine**, coarse

2 Materials and methods

2.1 Experimental apparatus

The overall experimental setup is shown in Fig. 1 and the experimental parameters and ranges are given in Table 1. Compressed air (Linde, Air Grade 0.1) served as the carrier gas for these experiments. The relative humidity (RH) of the carrier gas was controlled by diverting the bulk of the flow (190 sccm) through a $\sim$45 cm long, double-jacketed Pyrex glass flow tube that was partially filled with crushed ice. Air passing through the RH conditioning flow tube was saturated with the water vapour pressure over ice at the experimental temperature, thereby minimizing the potential for evaporation or condensation of water from or to the snow sample. Ozone (O_3) was generated by passing the remaining flow of dry compressed air (20 sccm) by a Hg Pen-Ray lamp. The ozone-rich air then passed through a 10 cm path-length quartz cell where the ozone concentration was determined from the attenuated output of a second Hg Pen-Ray lamp ($\lambda_{max} = 254$ nm). The ozone-rich air reconnected with the RH-rich air downstream of the RH conditioning flow tube.

The snow reaction chamber consists of a double-jacketed Pyrex glass vessel. Artificial snow was "poured" into the opening at the top of the reaction chamber to create a cylindrical snow sample $\sim$7 cm tall and $\sim$4 cm in diameter. Gases entered at the base of the snow sample through a 6.35 mm diameter inlet located on the side of the reaction chamber and were vented through a side-arm located just above the top of the snow sample. The reaction chamber was held at atmospheric pressure and a critical orifice controlled the flow of gases into the ion–molecule reaction region of the chemical ionization mass spectrometer (CIMS).

The samples were illuminated through a window at the top of the reaction chamber by the output of a 1 kW Xenon (Xe) arc lamp. A $\sim$20 cm path length water filter was placed between the arc lamp and the sample to remove infrared (IR) radiation to prevent over-heating of the sample, and a mirror directed the light onto the sample. In the majority of experiments a 310 nm long-pass filter (10 % transmission at 310 nm, measured using a commercial UV-VIS
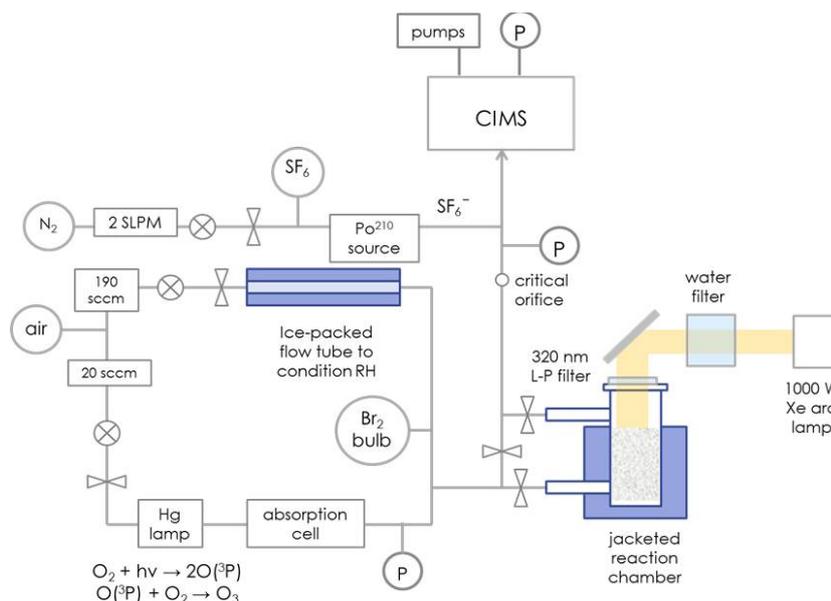
Fig. 1. Schematic of experimental apparatus.

spectrometer) was also placed over the quartz glass window. In some experiments, the 310 nm filter was replaced by a 360 nm long-pass filter (10 % transmission at 360 nm). Additional experiments were performed in which Br_2 or Cl_2 was introduced from a glass bulb manifold through the empty reaction chamber. Illumination did not lead to a measurable decrease in the Br_2 or Cl_2 signals in the absence of ozone for (a) the full spectral output of the Xe lamp with water filter and (b) the same as (a) but with a 310 nm or 360 nm long-pass filter.

The temperature of the reaction chamber and the RH conditioning flow tube were controlled by a Neslab chiller. The temperature in the reaction chamber was occasionally checked using a thermocouple and was typically ~ 5 K warmer than the chiller set point temperature. Reported temperature refers to the temperature of the snow within the reaction chamber.

2.2 Chemical ionization mass spectrometer

Gases were detected using a custom-built chemical ionization mass spectrometer (CIMS). The instrument, which is described in greater detail in Thornberry and Abbatt (2004), consists of two differentially pumped regions: the ion molecule region (IMR) and the multiplier chamber (MC). During operation, the pressures are 2.5 Torr and 2.5×10^{-6} Torr in the IMR and the MC respectively. The CIMS control box (Merlin QMS Controller) is interfaced to a PC operating using Merlin software from EXTREL (ABB Process Analytics, Inc.).

A trace flow of SF_6 (BOC, Grade 3.0), seeded in a 2 slpm dry N_2 flow (Linde, N_2 liquid Grade 4.8) was passed over a ^{210}Po ion source to produce the reagent ion, SF_6^-, via electron

attachment. A -112 V applied to the sheath surrounding the ion source helped direct the reagent ions into the IMR. Gas phase species produced by the experiment (O_3, Cl_2, BrCl and Br_2) were swept into the IMR by the carrier gas flow; charge-transfer reactions with the reagent gas occurred in the IMR:

$$X + SF_6^- \rightarrow X^- + SF_6 \tag{R6}$$

Thus, O_3, Cl_2, BrCl and Br_2 were detected at m/z 48, 70, 114 and 160 respectively. A scan time of 2 s was used. Ions entered the mass spectrometer through a pinhole which was biased to -14 V.

SF_6^- was chosen as the reagent ion because it can be used to simultaneously measure both O_3 and dihalogens. The reaction of SF_6^- with O_3 is very fast, near the collision rate (Huey et al., 1995). The reactions of SF_6^- with Br_2 and BrCl are also fast, but the reaction with Cl_2 is slower (Huey et al., 1995). Although the reaction between SF_6^- and water vapour is fairly slow, high mixing ratios of water vapour often preclude the use of SF_6^- as a reagent ion. However, at the cold temperatures used in these experiments and with the pressure drop to 2.5 Torr in the IMR, the water vapour pressure was low enough that the reagent ion signal remained sufficiently high.

2.3 Calibration

Calibrations for Cl_2 and Br_2 were performed routinely. Calibrations were performed in the absence of ozone with the reaction chamber bypassed. A small flow of either Cl_2 or Br_2 was released from a fixed-volume manifold to the main carrier gas flow (downstream of the RH conditioning flow tube,

as indicated in Fig. 1) and the pressure drop in the manifold as a function of time was converted to the equivalent concentration of either Br_2 or Cl_2 in molecules cm^{-3}.

The Cl_2 calibration bulb was prepared by delivering pure Cl_2(g) (Matheson) to an evacuated glass bulb. The Cl_2 in the bulb was then diluted with dry N_2 to a final mixing ratio on the order of 10^{-4}. The measured bulb pressures at the various dilution stages were used to determine the final mixing ratio, assuming ideal gas behaviour. The Br_2 calibration bulb was prepared by flash-freezing a small volume of liquid Br_2 in a round-bottom flask, pumping off the remaining vapour, then delivering Br_2(g) from the round-bottom flask into an evacuated glass bulb after warming the sample. The Br_2 in the bulb was then diluted with dry N_2 to a final mixing ratio on the order of 10^{-5}.

The intensity of the reagent ion (SF_6^-) varied somewhat from day-to-day. All signals were normalized to the simultaneously measured SF_6^- signal. During Cl_2 calibration, peaks at m/z 70, 72 and 74 respectively corresponding to $^{35}Cl^{35}Cl^-$, $^{35}Cl^{37}Cl^-$ and $^{37}Cl^{37}Cl^-$ were measured with the expected isotopic distribution. Similarly, during Br_2 calibration, peaks at m/z 158, 160 and 162 respectively corresponding to $^{79}Br^{79}Br^-$, $^{79}Br^{81}Br^-$ and $^{81}Br^{81}Br^-$ were measured with the expected distribution. Calibrations were not performed for BrCl, but we assume that the CIMS is equally sensitive to BrCl as it is to Br_2 (Abbatt et al., 2010). This assumption is based on their similar gas-phase electron affinities and their fast, collision-rate limited reaction with SF_6 (Huey et al., 1995).

The gas flow during calibration led to a CIMS signal in counts per second (cps) from which we determined sensitivity. Typically, the SF_6^- signal was between $(6–8) \times 10^4$ cps for the ion source. In all cases we normalized the measured ion signals to the SF_6^- reagent ion signal, which resulted in a unit-less intensity. For Br_2 and BrCl the normalized sensitivity was 1.7×10^{-16} per (molecule cm^{-3}) and for Cl_2 it was 5.8×10^{-17} per (molecule cm^{-3}). Using these calibrated sensitivities, we determined the concentration of dihalogens being released from the snow (molecules cm^3).

The limits of detection were determined from the signal-to-noise (S/N) ratio of the background signal during calibration. The noise was taken as the standard deviation of the background signal, measured for one minute (30 scans). For our operating conditions, our detection limits were $(2–3) \times 10^{11}$ molecules cm^{-3} for Br_2, $(1–2) \times 10^{11}$ molecules cm^{-3} for BrCl and $(3–5) \times 10^{11}$ molecules cm^{-3} for Cl_2.

2.4 Snow preparation

Artificial snow was prepared from a saline solution of NaCl(s) in 18 MΩ cm deionized water. The molar chloride to bromide ratio ($Cl^- : Br^-$) was varied by using different purities of NaCl(s); here we used reagent grade NaCl(s) (ACP Chemicals, 0.01% bromide impurity by weight) and

Fig. 2. Photographs of the artificial snow samples taken immediately after preparation.

high purity NaCl(s) (Fluka TraceSELECT®, < 0.001% bromide impurity by weight). Note that these salts possess molar $Cl^- : Br^-$ ratios that are much higher that the molar seawater $Cl^- : Br^-$ ratio of ∼650. The pre-freezing [NaCl(aq)] was 0.5 M for the majority of these experiments (and was varied between 0.1 and 1.0 M for select experiments). Initial solution pH was measured using a commercial pH electrode and adjusted using dilute H_2SO_4(aq) as needed. The pre-freezing pH was ∼2.3 for the majority of experiments. Unadjusted samples had an ambient pH ∼5.9. To prepare the snow, the nozzle of a mister bottle was used to disperse the saline solution into fine droplets which were directed into a dewar of liquid N_2. The contents of the dewar were then separated using a mesh sieve (hole diameter roughly 1 mm). The ice particles (i.e. the snow grains) captured by the sieve were mostly nonspherical (probably due to coagulation of individual droplets) and were estimated to be ∼0.5 mm in diameter. The ice particles that fell through the sieve were very fine and uniform to the eye (appearing as a fine powder), with an estimated diameter < 0.5 mm (see Fig. 2, left panel). This fine mode fraction was used for the majority of the experiments. All prepared snow was stored in amber glass jars in a freezer at 245 K for at least 1 day before use to allow the ice particles time to anneal. Coarse mode ice particles were prepared for some experiments by dropping saline solution directly into the liquid N_2 using a glass pipette. The resultant ice spheres were very roughly spherical and had a relatively wide size distribution (see Fig. 2, right panel). The mass of snow used was roughly ∼40 g for the fine mode samples and ∼50 g for the coarse mode samples. The snow samples filled a volume in the reaction chamber of ∼80 cm^3.
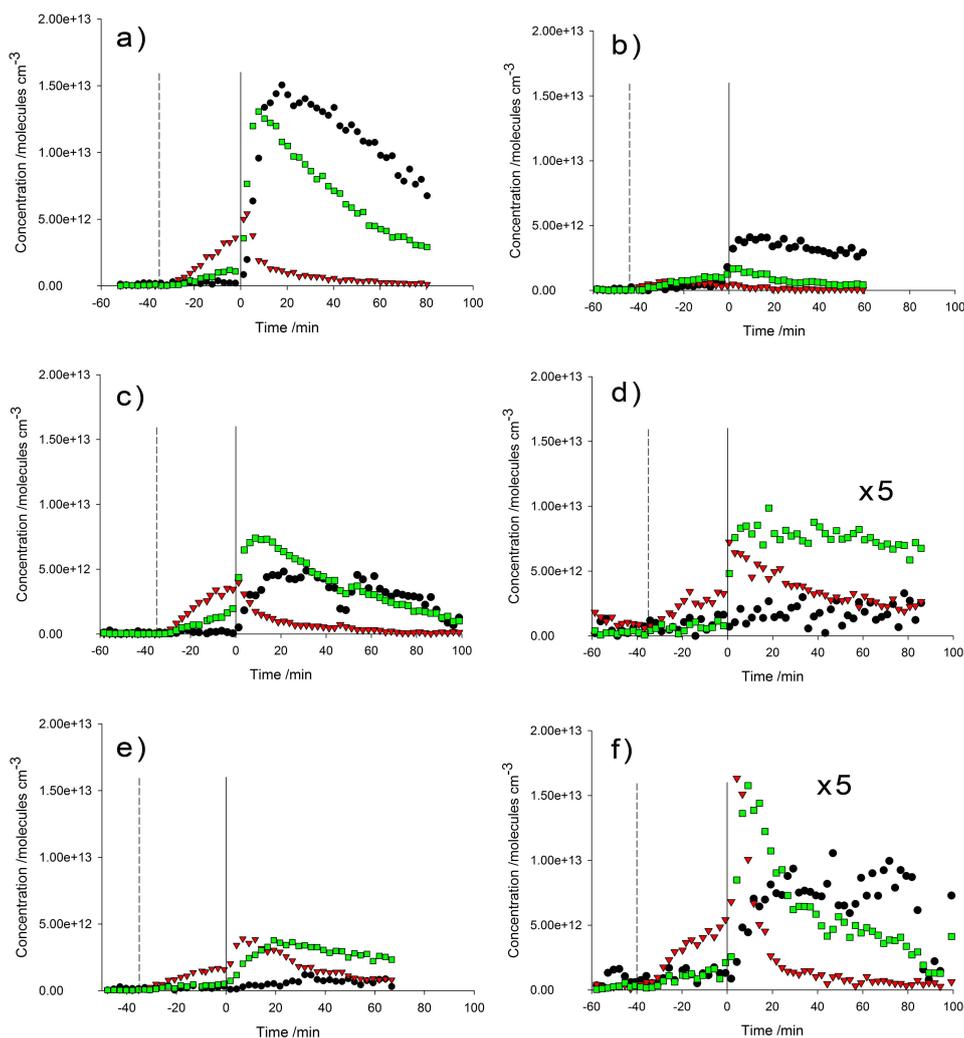
Fig. 3. Time evolution of the dihalogen concentrations during a typical experiment: Br_2 (red triangles), Cl_2 (black circles) and BrCl (green squares). Each point represents the average of a 2.5 min time bin (77 data points). The dashed line indicates the time at which the ozone generator was turned on and the solid line ($t = 0$) indicates the time at which the samples were illuminated. **(a)** BASE scenario conditions as in Table 1; BASE scenario conditions except with **(b)** high purity NaCl(s) ($Br^- < 0.001$ wt%) to prepare solution; **(c)** 360 nm long-pass filter; **(d)** coarse mode snow, scaled up by a factor of 5; **(e)** pre-freezing pH = 4.3; **(f)** snowpack T = 252 ± 1 K, scaled up by a factor of 5.

2.5 Snow characterization

To ensure that the artificial snow samples retained the same bulk composition as their initial solutions, some of the snow samples were melted and their ionic content was analyzed by ion-chromatography (IC). This was done separately for the coarse and fine fraction to ensure that the method of snow preparation and separation did not result in chemical fractionation. The analysis showed that the chloride concentrations remained unchanged due to freezing (for both the coarse and fine mode fractions). Unfortunately bromide concentrations could not be determined via the IC analysis due to interference from chloride.

3 Results and discussion

3.1 Photochemical chlorine production

Figure 2a shows results from a typical experiment under conditions that define the "BASE" scenario (which are shown in bold text in Table 1). Figure 3b–f demonstrate the effects of varying one parameter at a time from the BASE scenario. All the figures have the same vertical and horizontal scaling for ease of comparison and in all cases Cl_2 is shown as black circles, Br_2 as red triangles, and BrCl as green squares. To aid the interpretation of our results, we occasionally refer to the contribution of a given dihalogen to the total dihalogen sum $[Cl_2 + Br_2 + BrCl]$, henceforward the "Cl_2 fraction", "Br_2 fraction" and "BrCl fraction".

We observe that the *dark* exposure to ozone liberates Br_2 and in some cases BrCl from the snow (Fig. 3). Prior to illumination, $[Br_2]$ is greater than [BrCl], although the contribution of $[Br_2]$ to the total halogen release ($[Br_2]$ + [BrCl] + $[Cl_2]$) decreases slightly with time due to the slow depletion of snow bromide. Over the course of a typical BASE scenario experiment, we estimate that 10–15% of the total bromide content may react. As mentioned, the dark ozonation of frozen NaCl/NaBr solutions has been the subject of previous laboratory studies (Oum et al., 1998; Oldridge and Abbatt, 2011; Wren et al., 2010). These studies (Oldridge and Abbatt, 2011) suggest that the reaction proceeds in a liquid brine layer via a mechanism (Reactions R1–R4) that is similar to that occurring on/in the aqueous phase. The dark production of Br_2 and BrCl that we observe here is consistent with those studies.

Under all conditions studied here (i.e. shown in Fig. 3a–f), illumination of the snow sample (at $t = 0$) leads to a rapid increase in the concentration of all three dihalogens with the rate of increase most rapid for Br_2, slower for BrCl, and followed by Cl_2. No halogen production was observed when snow samples were illuminated in the absence of ozone. Cl_2 production (above the limits of detection) was only observed when both light and ozone were present.

The focus of this study is the accelerated halogen activation (particularly the Cl_2 activation) we observe when the halide-doped snow is exposed to ozone and light. In the following, we show that our observations support a snowpack "halogen explosion" – a chemical mechanism that is initiated by the photolysis of Br_2 or BrCl (formed via the dark ozonolysis of bromide) and perpetuated by the recycling of HOBr or HOCl back into the snowpack.

$$X_2 + h\nu \rightarrow X + X \tag{R7}$$

$$X + O_3 \rightarrow XO + O_2 \tag{R8}$$

$$XO + HO_2 \rightarrow HO_x + O_2 \tag{R9}$$

$$HO_x + h\nu \rightarrow OH + X \tag{R10}$$
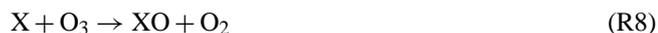
The mechanism shown above (Reactions (R7)–(R10)) has previously been proposed (Fickert et al., 1999; Fan and Jacob, 1992; Vogt et al., 1996; Foster et al., 2001; Simpson et al., 2007b; Abbatt et al., 2012; Tang and McConnell, 1996) to be important for activating bromine in the polar regions. Although laboratory studies have shown that HOBr will react with chloride or bromide at ice surfaces to give Br_2 or BrCl under certain conditions (Huff and Abbatt, 2002; Adams et al., 2002; Kirchner et al., 1997), the entire "halogen explosion" mechanism has not been directly investigated in controlled laboratory experiments using frozen substrates. Furthermore, this phenomenon has not been pursued as an important mechanism for activating chlorine in the form of Cl_2.

HOBr formed via R9 can oxidize Br^- in the condensed phase, leading to Br_2 and BrCl through Reaction (R3) and subsequent reactions. The HOBr can also oxidize Cl^- directly to give BrCl at the surface, which in turn can oxi-

dize Br^- to Br_2 (Adams et al., 2002). Cl radicals formed via the photolysis of BrCl (or eventually Cl_2) provide a route for HOCl formation, and the HOCl can oxidize Cl^- to give Cl_2 directly. In our experiments, we believe that $[Cl_2]$ grows more slowly because oxidation of Br^- will always be favoured over Cl^- when it is available and because Cl_2 formation requires prior BrCl formation (to provide Cl radicals via photolysis). Although molecular Cl_2 formation always occurs subsequent to BrCl formation, its observation contemporaneously to Br_2 shows that Br^- does not need to be exhausted for Cl_2 to form. The $[Br_2]$ and [BrCl] decrease rapidly once they have reached their respective maxima; this is presumably due to the fact that the snow is prepared from NaCl(s) containing only a small bromide impurity ($< 0.01\%$ Br^- by weight). Hence there is a small and finite amount of Br^- that can be liberated from the snow as either Br_2 or BrCl.

3.2 Direct observation of a snowpack halogen explosion

A direct role for reactive halogen species in the photochemical activation of halogens from the snow was explored in test experiments in which additional Br_2 gas was introduced to the reaction chamber via a fixed-volume glass bulb manifold coupled to the main gas flow. Figure 4a shows $[Cl_2]$, $[Br_2]$ and [BrCl] and Fig. 4b shows $[O_3]$ (expressed as a normalized signal) during such an experiment. The sample had been previously subjected to a typical experiment so that the concentrations of bromine containing products were very low, indicating a significant depletion of available bromide in the snow sample.

Consistent with the "halogen explosion" mechanism, Fig. 4a and b show that exposing this "pre-reacted" halide-doped snow to light, ozone and excess Br_2 leads to an increase in [BrCl] and $[Cl_2]$ (with [BrCl] increasing more rapidly than $[Cl_2]$) and a simultaneous decrease in $[O_3]$. Following an induction period as Br_2 is introduced from the bulb, its concentration is also anticorrelated to those of Cl_2 and BrCl. Production of BrCl and Cl_2 is not observed (or ceases) when either light, ozone or excess Br_2 is absent. Note that the $[Br_2]$ between ~ 60–80 min slowly decreases due to the fact that the additional Br_2 is being leaked from a glass bulb of decreasing pressure. Figure 4a illustrates that higher [BrCl] and $[Cl_2]$ are observed when higher $[Br_2]$ is present. Interestingly, in the absence of ozone, blocking and un-blocking the light has no noticeable impact on the dihalogen concentrations. As mentioned in Sect. 2, depletion of Br_2 or Cl_2 by photolysis alone was not important under our conditions.

3.3 Influence of snow Br^- / Cl^-

The important role that bromine activation plays in initiating the "bromine explosion" is also shown in experiments in which we reduced the snow Br^- / Cl^- ratio by an order of magnitude (through the use of high purity NaCl(s)).
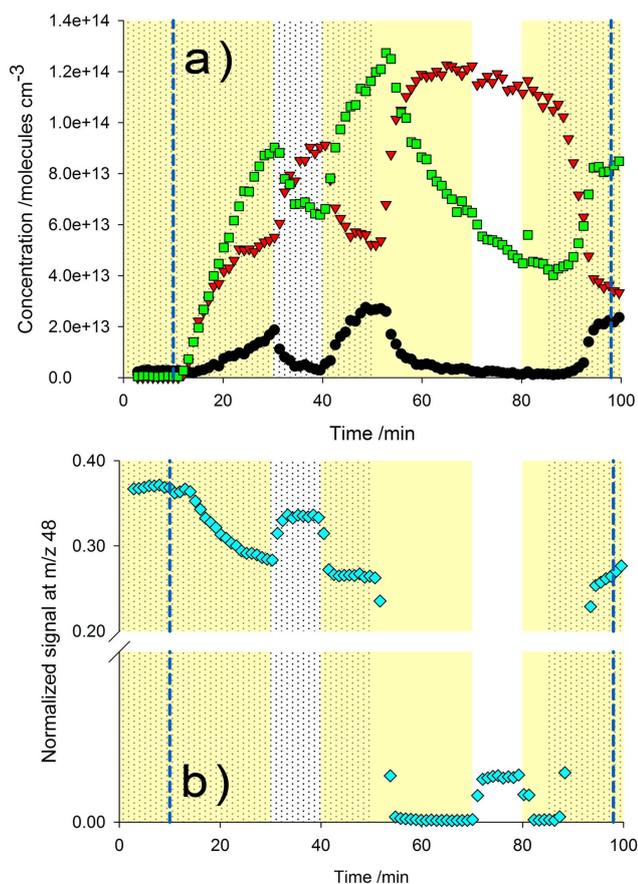
Fig. 4. Time traces of **(a)** dihalogen concentrations – Br_2 (red triangles), Cl_2 (black circles) and BrCl (green squares); and **(b)** ozone concentrations (light blue diamonds) during an experiment in which an additional flow of $Br_2(g)$ was delivered to the sample from a glass manifold (in the period of time indicated by the vertical blue dashed lines). The yellow areas indicate time periods during which the sample was illuminated. The dotted areas indicate time periods during which the ozone generator was switched on ([O_3] $\sim 1 \times 10^{14}$ molecules cm^{-3}). The experiment was run under BASE scenario conditions except high purity NaCl(s) ($Br^- < 0.001$ wt%) was used to prepare the solution. Each point represents the average of a 1 min time bin (30 data points).

Figure 3b shows that although the Cl_2 fraction is clearly enhanced relative to the BASE scenario under these conditions, the overall [Cl_2] is lower, despite the fact that the pre-freezing [Cl^-] is effectively unchanged. The fact that reducing the Br^-/Cl^- ratio while keeping pre-freezing [Cl^-] constant leads to a decrease in Cl_2 is consistent with a snowpack "halogen explosion" that requires the initial formation of Br_2 and BrCl.

3.4 Wavelength dependence

Support for a snowpack "halogen explosion" driven by halogen photolysis is also provided by the observed wavelength dependence. Replacing the 310 nm long-pass filter with a

360 nm long-pass filter is expected to reduce the rate constant for dihalogen photolysis (J_6) for Cl_2 ($\lambda_{max} = 330$ nm) much more than for BrCl ($\lambda_{max} = 370$ nm); the J_6 for Br_2 ($\lambda_{max} = 420$ nm) should be the least effected (Finlayson-Pitts and Pitts, 2000). Indeed, comparison of Fig. 3c with Fig. 3a shows that use of the 360 nm long-pass filter leads to lower yields of all three dihalogens, which can be attributed to less HOBr or HOCl formation via Reactions (R6)–(R8) under these conditions. Furthermore, the slower evolution of the Cl_2 fraction under these conditions is consistent with lower yields of Cl radical due to the fact that the J_6 for BrCl and Cl_2 photolysis are lowered to a greater extent than the J_6 for Br_2. The fact that we observe photochemical halogen activation under both illumination conditions also allows us to conclude that OH(g) formed via O(^{1}D) from gas phase ozone photolysis is not an important oxidant in our experiments.

3.5 Surface area dependence

Central to the "halogen explosion" mechanism is the recycling of gas phase products back into the snow. Hence, halogen activation via this mechanism should be enhanced when a larger surface area is available, and Cl_2 production should be most affected since it relies solely on the photochemical pathway (i.e. Br_2 and BrCl can both be formed in the dark). The influence of available surface area was investigated by performing experiments using a coarse mode snow (see Fig. 2, right panel and Fig. 3d), with all other conditions the same as in the BASE scenario. Comparison of Fig. 3a and d shows that the dihalogen production is indeed suppressed when the available surface area is reduced. In particular, the Cl_2 fraction evolves very slowly for the coarse mode experiments; the BrCl fraction remains high for the duration of the experiment. We note that the larger yields we observe when a greater surface area is present could also support a reaction taking place at the frozen surface. Halide ions are known to have a positive surface affinity (Jungwirth and Tobias, 2006) and thus have the potential to be involved in interfacial reactions (Knipping et al., 2000).

3.6 pH dependence

Dihalogen formation was reduced when the pre-freezing pH was increased to ~ 4.3 (see Fig. 3e). The dark evolution of [Br_2] was the least affected, while the production of [Cl_2] upon illumination was dramatically suppressed. At a pre-freezing pH of 5.9, any dihalogen production lay below the detection limits. The strong pH dependence for Cl_2 production may indicate that in the Cl^- analog of Reaction (R3), an initial protonation of HOCl to form H_2OCl^+, is the rate-limiting step (as suggested for the aqueous phase by Donaldson et al., 1997). A mechanism involving HOCl reaction with H^+ followed by reaction of H_2OCl^+ with Cl^- is also consistent with the lack of temperature dependence on Cl_2 yields for temperatures above the eutectic (vide infra).

A strong acidity dependence has also been reported for the $HOBr + Br^-$ Reaction (R3) in the aqueous phase (Fickert et al., 1999), although the acidity dependence is expected to be weaker than that for chlorine. Although studies of HOBr reactions with frozen halides substrates have shown that Br_2 and BrCl will form under a wide range of acidities (Huff and Abbatt, 2002; Adams et al., 2002), we note that those studies were carried out at temperatures below the eutectic for which the ice surface should be quite different than in the present experiment and for which we also see little halogen production (see Sect. 3.8).

3.7 HO_x and O_3

The "halogen explosion" mechanism requires an HO_2 source to be present in the snow interstitial air. Snowpacks are now known to be sources of OH, HO_2 and small organics such as HCHO (Domine and Shepson, 2002; Grannas et al., 2007). Indeed, using the same experimental set-up and similar illumination conditions Gao et al. (2012) measured the release of VOCs from natural snow samples collected from urban, rural and remote sites. Although organics were not intentionally introduced to our samples, it is well known that reagent grade salts and laboratory deionized water contain organic impurities (Gao and Abbatt, 2011). It is also possible that gas phase organics or acids present in the room contaminated our samples during preparation (fast-freezing in liquid N_2). Thus, upon sample illumination, it is possible that active snowpack chemistry leads to HO_x formation. Additionally, the oxidation of VOCs by Cl radicals is known to lead to the formation of HO_2 and small aldehydes (i.e. HCHO), which are themselves precursors for HO_x (Simpson et al., 2007b). The production of HONO and NO_x via the photolysis of a nitrate impurity in the snow could also play an important role in perturbing the HO_x budget. A few other possibilities for HO_x formation, including the photodissociation of surface adsorbed O_3 or reactions involving thermally-hot $O(^3P)$, are considered in the Supplement.

Figure S1 in the Supplement shows that reducing the ozone concentrations leads to an overall decrease in the halogen production. Figure S2 shows that the evolution of the dihalogen fractions with time is independent of gas phase $[O_3]$ over this range, suggesting that the chemical mechanism is not affected by changing the ozone concentrations over the range.

3.8 Brine chemistry

An important question concerns the environment where the chemistry is occurring. When salt solutions freeze, salt ions are excluded from the growing ice matrix into an increasingly concentrated liquid brine. Thus, it has been well-established that sodium halide solutions will contain small liquid fractions down to temperatures at, or even slightly below, their eutectic temperatures (Koop et al., 2000). Together, the temperature and salt concentration dependence that we observe suggests that the photochemical halogen production takes place in such a concentrated liquid brine located at the surface of the snow grains. The reasons for this are as follows. At temperatures near or below the NaCl-water eutectic of 252 K (Koop et al., 2000), the brine fraction is negligible. Under these conditions, illustrated in Fig. 3f, we find dihalogen production to be significantly suppressed, indicating that chloride availability in a liquid brine is key to this mechanism. At temperatures below the eutectic, chloride will be precipitated in any remaining brine, leading to chemical fractionation. We observe that the Cl_2 fraction grows more slowly at colder temperatures (see Fig. S3a in the Supplement), indicating that the bromide/chloride ratio in the existing brine may be affected by the removal of chloride via precipitation. Fractionation of bromide with respect to chloride has previously been shown to affect heterogeneous chemistry on frozen halide surfaces (Lopez-Hilfiker et al., 2012). Huff and Abbatt (2000) have reported the only laboratory study of HOCl interactions with halide-containing ice surfaces. They also report no reaction for HOCl or Cl_2 with frozen NaCl(aq) ice films at temperatures below the NaCl-water eutectic.

The influence of temperature on the Cl_2 production is further illustrated in Fig. 5, which shows the total Cl_2 yield in 50 minutes of illumination as a function of snow sample temperature. The yields were calculated by integrating the Cl_2 concentration-time signal to 50 minutes and scaling by the flow rate. Interestingly, the Cl_2 yields are independent of temperature above the eutectic. Thermodynamic models for calculating brine concentrations (Cho et al., 2002; Kuo et al., 2011) predict that the brine halide concentrations are a strong function of temperature. Thus, the temperature independence we observe suggests that Cl_2 production is independent of brine $[Cl^-]$ (which is quite high in the brine due to this temperature-dependent freeze-concentration). This observation is consistent with initial protonation of HOCl being rate-limiting, as discussed in Sect. 3.6, although given its complexity, the exact mechanism cannot be confirmed.

Changing the pre-freezing [NaCl] concentration was found to have an effect on the total dihalogen concentrations (Fig. S4 in the Supplement) but no effect on the time evolution of the dihalogen fractions (Fig. S5 in the Supplement) over the range 0.1–1.0 M. This likely indicates that (a) fractionation of the halides does not occur during freezing and the Br^-/Cl^- ratio in the brine is the same for the three concentrations studied; (b) the chemical mechanism remains the same in all three cases; and (c) the difference in the absolute dihalogen production is due to differences in the total halide content (i.e. brine fraction).

4 Conclusions

We have observed accelerated halogen activation, in particular Cl_2 activation, from artificial saline snow in the presence
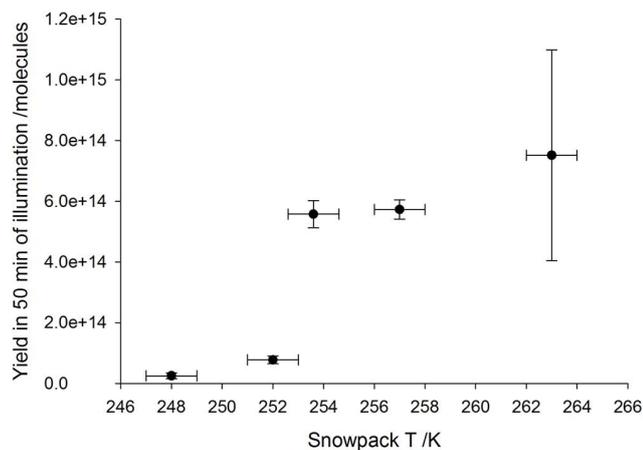
Fig. 5. Dependence of the chlorine (Cl$_2$) yield as a function of snowpack T. Vertical error bars represent the range from two trials. Horizontal error bars represent the estimated uncertainty in the snowpack T. The yields were calculated by integrating the Cl$_2$ concentration-time signal to 50 min and scaling by the flow rate.

of ozone and radiation of actinic wavelengths. Illumination of the snow samples was found to lead to the rapid release of Br$_2$, then BrCl, and ultimately the release of Cl$_2$. Our observations are consistent with chemistry occurring in a concentrated liquid brine located at the surface of the snow grains, with chlorine activation only occurring at temperatures above the eutectic (252 K). We found the production of the dihalogens to be favoured under acidic conditions, more so for Cl$_2$ than for Br$_2$. Finally our results show that photochemical halogen activation, particularly chlorine activation, is enhanced when a larger surface area is present. Provided a HO$_x$ source is present, the results are most consistent with a 'halogen explosion' mechanism in which HOBr and HOCl are formed via the gas phase reaction of O$_3$ by halogen radicals and are recycled back into the snow to oxidize Br$^-$ or Cl$^-$.

4.1 Atmospheric implications

Considerable debate has centred on where bromine activation occurs in the polar regions, with proposals that first-year sea ice (Simpson et al., 2007a); frost flowers (Rankin et al., 2002; Kaleschke et al., 2004); saline snowpack (Morin et al., 2008) and blowing salty snow (Yang et al., 2010; Jones et al., 2009) play an important role. These substrates have variously been proposed for their high salinity, large surface area or enriched bromide content.

Given the strong acidity and surface area requirement we observe for chlorine production, we propose that aged saline snow (i.e. at a coastal location) will be most important for chlorine activation in the polar boundary layer. Although the pH at the air–ice interface has not been well-constrained, the bulk pH of seawater and seawater-derived substrates (frost flowers, first-year sea ice, brines) is alkaline (pH ~8.3) and

is buffered against pH change by the carbonate system. Furthermore, work from our group suggests that the pH at an air–ice interface is largely unchanged during freezing (Wren and Donaldson, 2012a) and that the frozen seawater surface maintains some buffering capacity (Wren and Donaldson, 2012b). Snowpacks at coastal locations can achieve much lower pH values (~4.5) if they are aged (i.e. have been acidified by atmospheric trace acids) (Jacobi et al., 2012; de Caritat et al., 2005). The pH of snow at inland sites may be even lower, but these samples may also be limited in their halide content. Acidification of natural snow samples may also lead to a very low local surface pH which is not captured by the bulk, melted pH. The relatively low surface areas of first-year sea ice and even frost flowers (Domine et al., 2005; Obbard et al., 2009) also preclude them from playing an important role in activating chlorine via the process observed in this study. In our study, we provide strong evidence for active chemistry occurring within the interstitial air of snow that is enhanced when a larger surface area is present. The proposal that aged, acidic snow is most relevant to halogen activation is consistent with very recent measurements by Pratt et al. (2013) showing efficient bromine release from natural snow samples but not from sea ice or brine icicles.

Halide concentrations in coastal snowpacks can vary widely, with average chloride concentrations ranging from $< 1000 - > 33\,000\,\mu g\,L^{-1}$ and average bromide concentrations ranging from 30–$450\,\mu g\,L^{-1}$ for snow over first-year ice (and lower for snow on land or multi-year ice) (Jacobi et al., 2012; Krnavek et al., 2012). However, due to freeze-concentration effects, the concentration of halides available at the surface of real snow grains may be quite high, and, assuming thermodynamic models correctly treat such systems, should be a function of temperature rather that total salinity (Kuo et al., 2011; Cho et al., 2002). Furthermore, snow metamorphism may help mobilize the halides within the snowpack (whereas our artificial snow may contain trapped liquid pockets due to the very harsh freezing conditions).

Observation of both Br$^-$-enriched and Br$^-$-depleted snow have been observed in the field, with enrichments attributed to non-sea salt contribution from HOBr and depletions due to bromine activation chemistry (Jacobi et al., 2012; Krnavek et al., 2012). The dependence on the Br$^-$/Cl$^-$ ratio we observe is quite interesting. On the one hand, when a large amount of bromide is available, it will preferentially be oxidized over chloride, and so production of Br$_2$ and BrCl should dominate. High bromide concentrations will also react at the surface with Cl$_2$ and BrCl to form BrCl or Br$_2$ respectively, as has been observed by laboratory experiments (Huff and Abbatt, 2000; Adams et al., 2002; Huff and Abbatt, 2002). However, our experiments do suggest that molecular Cl$_2$ is formed even when bromide is still present. On the other hand, we find that chlorine production decreases when the bromide/chloride decreases, which implies the involvement of HOBr formed via prior bromine activation. Thus, a certain amount of bromide may be necessary to initiate this

chemistry. The photochemical halogen activation we observe is very efficient and should lead to rapid depletion of snow bromide. The high surface area of snow, together with bromide's strong surface affinity (Jungwirth and Tobias, 2006) should particularly favour rapid depletion of snow bromide.

An important question concerns the role that BrCl plays in contributing to the Cl radical budget and to further chlorine activation. Our results show that a process involving light and ozone could liberate large amounts of BrCl from aged, surface snow, which will release Cl radicals upon photolysis. BrCl is important here, not only as a direct Cl radical source, but as a precursor to HOCl formation, which we suggest leads to Cl_2 formation. Generally consistent with our study, observations of Br_2 and BrCl over snow at Alert show similar trends for both dihalogens, with Br_2 reaching as high as 25 ppt and BrCl reaching as high as 35 ppt (Foster et al., 2001; Spicer et al., 2002). Notably, BrCl was not observed above the 2 ppt detection limit at the beginning of the campaign (in total darkness) but was observed almost continuously midway through the campaign and onwards; Cl_2 was not observed above the 2 ppt detection limit. The later appearance of BrCl may be related to both bromide depletion in the snow and the increasing irradiance during the campaign.

Our results implicate the need for a "seed" reactive halogen source as well as a sustained HO_x source within the snow. Although the relatively high ozone concentrations were likely responsible for the formation of "seed" Br_2 and BrCl in this study, OH produced within natural snowpacks may play an important role in the initial formation of these species in the field (Pratt et al., 2013). This indicates that nitrate snowpack photochemistry and organic release from the snow – both of which affect the HO_x budget – are likely intimately linked to halogen activation; further research is required to improve our understanding of the highly coupled air–ice interactions occurring within the snowpack.

The polar regions, and particularly the Arctic, are strongly affected by our changing climate. In the Arctic, a large decrease in sea ice extent has been accompanied by an increase in the relative area of first-year sea ice compared to multi-year ice (Maslanik et al., 2007). A long-term increase in the frequency of ozone depletion events during early spring may be attributed to this change (Oltmans et al., 2012). Given that snow lying on first-year sea ice has a higher salinity, halogen chemistry is expected to be affected as the Arctic succumbs to further changes. Our study contributes significantly to our growing understanding of halogen activation processes and how they might be impacted in a changing world. Further research is required using authentic snow and ice substrates to support the work presented here.

Supplementary material related to this article is available online at http://www.atmos-chem-phys.net/13/ 9789/2013/acp-13-9789-2013-supplement.pdf.

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