

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/230780981>

Freeze-Induced Formation of Bromine/Chlorine Interhalogen Species from Aqueous Halide Ion Solutions

ARTICLE *in* ENVIRONMENTAL SCIENCE & TECHNOLOGY · AUGUST 2012

Impact Factor: 5.33 · DOI: 10.1021/es301988s · Source: PubMed

CITATIONS

4

READS

68

2 AUTHORS:



Ruairi O Concubhair

University College Cork

3 PUBLICATIONS 20 CITATIONS

SEE PROFILE



John R Sodeau

University College Cork

182 PUBLICATIONS 2,738 CITATIONS

SEE PROFILE

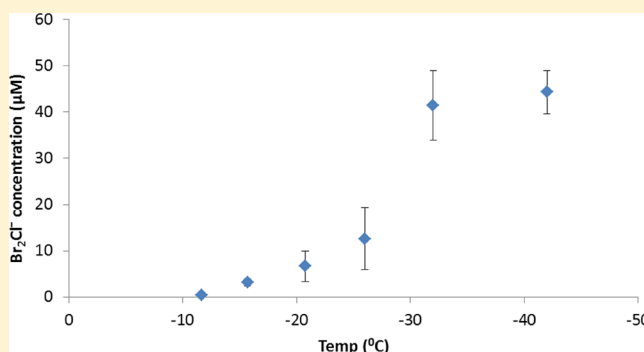
Freeze-Induced Formation of Bromine/Chlorine Interhalogen Species from Aqueous Halide Ion Solutions

Ruairí O'Concubhair and John R. Sodeau*

Department of Chemistry, University College Cork, Cork, Ireland

S Supporting Information

ABSTRACT: Both gaseous bromine and bromine chloride have been monitored in polar environments and implicated in the destruction of tropospheric ozone. The formation mechanisms operating for these halogen compounds have been suggested previously. However, few laboratory studies have been performed using environmentally relevant concentrations of bromide and chloride ions in polar ice mimics. In aqueous solutions held at room temperature, previous studies have shown that the major product is the Cl_2Br^- trihalide ion when solutions of bromate, hydrochloric acid, and bromide ions are left to equilibrate. In contrast, the results of the cryochemical experiments presented here suggest that the dibromochloride ion (BrBrCl^-) is the major product when solutions of bromate, sulfuric acid, bromide, and chloride ions are frozen. Such a species would preferentially release bromine to the gas phase. Hence, similar halide starting materials form structurally different trihalide ions when frozen, which are capable of releasing differing active halogens, BrCl and Br_2 , to the gas-phase. This is a potentially important finding because Br_2 is photolyzed more readily and to longer wavelengths than BrCl and therefore the efficiency in forming products that can lead to ozone destruction in the atmosphere would be increased. Evidence is provided for the mechanism to occur by means of both the freeze-concentration effect and the incorporation of ions into the growing ice phase.



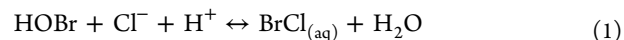
INTRODUCTION

Measurements in the Arctic troposphere have shown that during polar springtime large concentrations of ozone are destroyed in what are known as ozone depletion events (ODE's), whereas atmospheric mercury depletion events (AMDE's) are also known to occur during the same periods.¹ Furthermore, increases in atmospheric bromine concentrations, often termed bromine explosions, occur concurrently with these events.² In fact, there is considerable evidence for anticorrelations between bromine and ozone/mercury levels over these time periods, which suggests that one or more bromine species is/are the cause of the losses.^{3,4} Indeed Barrie et al.⁵ have suggested a catalytic cycle involving Br and BrO radicals, which results in the depletion of ozone and that these radicals may also oxidize and remove mercury from the troposphere.⁶ However, a recent laboratory study indicates that a dark oxidation transformation process for mercury species may also be important in environments containing water-ice.⁷

It has been suggested by Neumann et al.⁸ that the importance of the Br_2 and BrCl halides with regards to daytime Arctic photochemistry may be overestimated due to the conversion of HOBr to Br_2 on the surfaces of inlets, thereby contributing to increased observations of Br_2 during daytime. In addition, BrCl was found to be below the detection limit throughout the vertical profile in the Arctic. However, a recent study by Liao et al.⁹ reports that Br_2 is observed in significant

mixing ratios at night while little BrCl was observed. This suggests that Br_2 is formed preferentially over BrCl at night in the Arctic.

The formation of interhalides that can destroy ozone have been described by Vogt et al.¹⁰ previously and they demonstrate how such species can form and dissociate in aqueous solutions to produce bromine, which may subsequently diffuse into the atmosphere.



The reaction scheme depicted as reactions 1–4 represents a possible mechanism by which the reactive interhalide ion, Br_2Cl^- , and bromine is formed. The aqueous bromine product of reaction 4 may diffuse from solution into the atmosphere (as with the BrCl product in reaction 2). It could then photolyze to

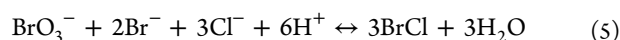
Received: May 17, 2012

Revised: August 27, 2012

Accepted: August 31, 2012

Published: August 31, 2012

produce active Br, which can readily destroy tropospheric ozone.¹¹ This scheme, for autocatalytic Br activation, places emphasis on Br₂Cl[−] formation rather than the alternate trihalide ion, BrCl₂[−].¹⁰ A study conducted by Liu and Margerum¹² has shown that when room temperature solutions containing 1 M HCl and stoichiometric amounts of sodium bromide and sodium bromate (reaction 5) are analyzed that the principal product formed is BrCl₂[−]. From constructed computer models of the homogeneous species distribution in room temperature solutions over the pH range of 0–7 and a chloride concentration of 1 M, it was observed that the BrCl₂[−] interhalide ion is formed preferentially over the Br₂Cl[−] interhalide counterpart. In the experiments conducted in this study, sulfuric acid and sodium chloride were substituted for hydrochloric acid in order to alter pH and the chloride concentration individually.^{13,14}



However, there have been no previous studies conducted into whether the formation of the Br₂Cl[−] or BrCl₂[−] interhalides are favored at concentrations mimicking those found in polar environments or indeed at relevant temperatures when water–ice is present.

Recently, low-temperature (<−15 °C) freezing chemistry has been reported to cause the acceleration of several reactions relevant to polar atmospheric chemistry.^{15–18} For example, UV spectroscopic studies have shown that interhalide formation is promoted by the freezing of various halide ion solutions.^{19,20} The mechanism for the formation of the interhalide ions, such as ICl₂[−] and IBr₂[−], is believed to be due, mainly if not exclusively, to the well-known freeze-concentration effect. This phenomenon causes reaction rates to be accelerated upon the process of freezing because when solutions are cooled, microscopic regions of unfrozen liquid, termed micropockets, microveins, or triple junctions become integral parts of the overall ice structure.²¹ Solutes are rejected from the growing ice-phase and become concentrated in these pockets, thereby leading to an acceleration of reaction rates. An investigation by Abbatt et al. using other experimental techniques has also shown that when gas-phase ozone was exposed to frozen aqueous NaCl/NaBr solutions gas-phase bromine was formed through a suspected freeze-concentration effect.²²

During the freezing process, small amounts of solutes may be incorporated into the ice crystals, and variations in the incorporation of cations and anions between the solid component and the unfrozen solution may generate an electric potential. Thus, if the anion is preferentially incorporated into the growing ice phase a negative charge is generated within the ice but if the cation is preferentially incorporated a positive charge is generated.^{23,24} The differing incorporation of ions into the growing ice phase may affect the chemistry of reactions in the unfrozen micropockets.

As shown in reaction 1, a key reagent in the formation of the bromine chloride interhalide ions is HOBr. However, hypobromous acid is difficult to isolate due to its instability and thus hypobromous acid was generated in situ by the reaction between bromate and acid.^{22,25,26} Hypobromous acid itself has previously been shown to quite soluble in sulfuric acid solutions representative of upper tropospheric and lower stratospheric aerosol composition.²⁷ Concentrations of hypobromous acid have not been accurately quantified in the polar regions due to its reaction on surfaces to form bromine.⁸

However, a recent study using a mist chamber has reported that the average daytime mixing ratio of HOBr is 10 pptv.⁹

As mentioned above, several published reports have indicated that the freezing process can result in rate accelerations and alternative reaction pathways being followed from those observed in room temperature solutions. In fact, freezing a solution can result in the concentrating of solutes by a factor in excess of 1000 times due to the existence of micropockets.²⁸ Therefore, the initial experiments performed here focused on determining whether freezing caused acceleration of interhalide formation or alternative reaction pathways at low concentrations of reagents.

■ EXPERIMENTAL SECTION

Sodium chloride (NaCl Sigma 99.5%), potassium bromide (KBr Sigma 99%), sodium bromate (NaBrO₃ Sigma 99.5%), and sulfuric acid (H₂SO₄ Sigma 97–95%) solutions were made up in deionized water and contained in 50 mL round-bottom flasks. The concentrations of Cl[−] and Br[−] used in this study were 0.57 M NaCl and 0.82 mM KBr, whereas bromate concentrations of 41 μM were also utilized. The pHs of solutions were adjusted to 2.5 unless otherwise stated. All solutions unless otherwise stated were then frozen in an ethanol bath using a Neslab CC-100 cryocooler to −30 °C for one hour. This temperature was chosen to mimic temperatures in polar regions during the winter months. Following removal from the freezing bath, the solutions were thawed using a warm water bath (25 °C) and analyzed immediately using a Thermo Scientific Evolution 60S UV–vis spectrophotometer. The solutions were found to be stable for at least one hour after freezing. The nonfrozen solutions were maintained at room temperature for one hour and assessed following the analysis of the frozen solutions. All flasks were wrapped in aluminum foil in order to prevent photolysis. Sulfuric acid was employed for acidification of the solutions because its conjugate bases are unlikely to act as oxidizing agents. Spectral deconvolution was performed using Thermo Galactic Grams AI software and the peak wavelengths measured are given in Table 1. Further information on the reaction mechanism was obtained by omitting chloride or bromide ions from the initial mixtures. Also, equimolar ammonium chloride (NH₄Cl Sigma 99.8%) solutions were synthesized and substituted where appropriate for sodium chloride.

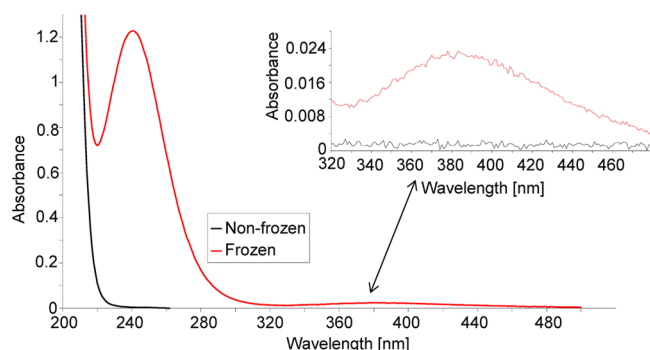
■ RESULTS AND DISCUSSION

New Product Pathway upon Freezing. No products, detectable by UV spectroscopy, were formed in nonfrozen solutions after a period of one hour. However, solutions which were frozen for 1 h at −30 °C showed the formation of UV absorption peaks at 240 and 390 nm as seen in Figure 1. The former wavelength represents the approximate midway point between the 232 and 245 nm bands corresponding to the previously assigned absorptions for BrCl/BrCl₂[−] (232 nm) and Br₂Cl[−] (245 nm) as indicated in Table 1. The feature at 390 nm corresponds to Br₂ but is also close to the second characteristic absorption band for Br₂Cl[−], which is located at 381 nm. The possible presence of either aqueous molecular chlorine or the trichloride ion in the spectra is difficult to ascertain due to the lack of discernible features for their known absorptions at 232 and 325 nm, respectively. It should be noted that the UV data measured previously for both BrCl₂[−] and Br₂Cl[−] does not distinguish between an XXY[−] type trihalide ion or its YXY[−]

Table 1. Absorption Wavelength Maxima and Molar Absorption Coefficients of Primary Interhalide Species in Aqueous Solution^{12a}

species	λ (nm)	ϵ (M ⁻¹ cm ⁻¹)
BrCl ₂ ⁻	343	312
	232	37 200
BrCl(aq)	343	70
	232	650
Br ₂ Cl ⁻	381	288
	245	24 900
	232	17 000
Br ₂ (aq)	390	175
	232	400
HOBr(aq)	260	100
	232	58
Br ₃ ⁻	362	850
	266	40 900
	232	2500
	220	10 400
Cl ₂ (aq)	325	70
	232	0
	<210	>290
Cl ₃ ⁻	325	180
	232	8800
	220	10 400

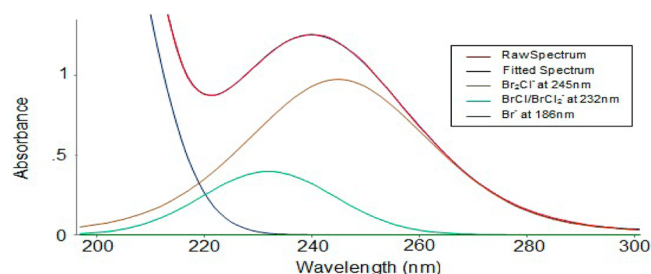
^aConcentrations of the Br₂Cl⁻ interhalide ion were obtained by calculating the concentration from the absorption band maximizing at 245 nm following spectral deconvolution of the spectra. The limit of detection (Average +3*standard deviation of 10 blanks) for Br₂Cl⁻ was found to be 0.3 μ M. The R² values for each of the fitted spectra were >0.999. All error bars in the figures are twice the standard deviation of a minimum of four repeated measurements.

**Figure 1.** Comparison of frozen (red) and nonfrozen (black) UV-vis spectra of 0.57 M NaCl, 0.82 mM KBr, 41 μ M NaBrO₃, at pH 2.5 (path length = 1 cm).

counterpart. Although, according to an ab initio molecular orbital study carried out by Ogawa et al.,²⁹ when Y is heavier than X, the (X–Y–X)⁻ and (Y–Y–X)⁻ isomers are calculated to be more stable than their counterparts. Therefore, in the case of the bromide and chloride ions, the (Cl–Br–Cl)⁻ and (Br–Br–Cl)⁻ isomers are likely to be formed preferentially in solution.

From spectral deconvolution of the spectra using Grams AI software and the wavelengths and molar absorption coefficients shown in Table 1, it was determined that the peak at 240 nm incorporated absorption bands at 232 and 245 nm as shown in Figure 2.

Furthermore, as seen in Figure 1, the absorption band apparent at 381 nm (Br₂Cl⁻) in the frozen spectra but with no

**Figure 2.** Spectral deconvolution of the peak at 240 nm.

significant band at 343 nm (BrCl/BrCl₂⁻) suggests that Br₂Cl⁻ is formed preferentially over BrCl₂⁻ by the freezing process. Further evidence for the formation of the dibromochloride interhalide is that the absorbance value measured at 245 nm is approximately 100 times greater than that observed at 381 nm. This observation is in line with the absorption coefficient data shown in Table 1 for Br₂Cl⁻ at 245 and 381 nm. The above results indicate that interhalide species formation may be accelerated at low bromate and bromide concentrations due to the freezing process. In addition, it was observed that the favored product formed was dissimilar from previous reports of experiments and computer models of the aqueous system. In view of this novel finding, the possible mechanisms responsible for the observed behavior were probed further.

Role of Freeze-Concentration and Freeze-Potential in the Chemistry. To determine the mechanism by which freezing caused the acceleration of the reactions, the temperature-dependence of the product(s) formation was investigated to assess whether a freeze-concentration process was causing the effect. Hence, the UV spectra of solutions were studied after cooling to various temperatures between 0 °C and -42 °C to determine whether the actual temperature of freezing plays a role either in the acceleration or the nature of the products formed. In general, the lowest temperatures will promote the smallest liquid-containing micropockets. Hence, at the lower temperatures, a greater concentration effect occurs.³⁰ The eutectic temperature for the sulfuric acid–water system is believed to be -73 °C and liquid sulfuric acid has been observed in the triple junctions of Antarctic ice.³¹ Furthermore, a study by Koop et al.³² has shown that that ice made from solutions containing NaCl and NaBr have a liquid component to temperatures below -50 °C. Thus, under the conditions utilized in the current study, an unfrozen micropocket or triple grain will likely remain within the ice structure at temperatures of -42 °C and warmer.

As can be seen from Figure 3, which uses absorbance values at 245 nm following spectral deconvolution to calculate the Br₂Cl⁻ concentration, the formation of the dibromochloride ion increases as the temperature is decreased. These results suggest that a freeze-concentration effect is occurring, which begins to maximize at -32 °C, after which point little, if any, additional product appears to form. Absorbance values at 232 and 245 nm are shown in Figure S1 of the Supporting Information.

Liu and Margerum¹² showed, using high concentrations of reagents (1 M [Cl⁻], 1 M [H⁺] and stoichiometric amounts of Br⁻ and BrO₃⁻), that the dichlorobromide ion was formed rapidly without the need for freezing. Observations from the current study employing low concentrations of reagents showed that such nonfrozen solutions do not give rise to detectable UV spectra as an indication of interhalide ion

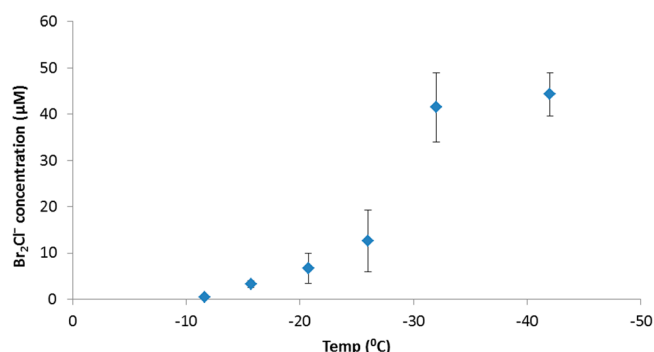


Figure 3. Effect of temperature on the formation of Br₂Cl⁻.

formation. However, freezing the solutions does result in interhalide formation. It therefore follows that a freeze-concentration effect represents at least one cause of interhalide formation in the systems studied here. However, other types of freezing mechanisms may be occurring in conjunction with a freeze-concentration effect and these were investigated as outlined below.

A number of experiments were conducted to examine whether or not the freeze-induced formation of Br₂Cl⁻ was stimulated by catalysis of reactions on ice surfaces. Hence, crushed ice to increase reaction surface area was added to solutions and the flasks were held at a constant temperature of -1 °C for one hour. No interhalide ion formation resulted, which suggests that no catalysis was occurring on the surface of the ice.

Further experiments were conducted whereby ammonium chloride was substituted for sodium chloride in the solution. The rationale behind these experiments is that ice becomes *negatively charged* during the freezing of dilute alkali chloride solutions because of the selective inclusion of chloride ions into the solid ice phase. However, ice becomes *positively charged* during the freezing of NH₄Cl due to the selective inclusion of NH₄⁺ ions into the solid ice phase.³³ Therefore, replacing sodium chloride with ammonium chloride allowed for the determination of whether the incorporation of the chloride ion in the growing ice phase was occurring.

The results of these experiments showed that the effect of replacing sodium chloride with ammonium chloride (pH 2.5) leads to a very significant reduction in the level (from 4.2 to 0.9 μM) of Br₂Cl⁻ and the absorbance at 232 nm (Figure S2 of the Supporting Information). This reduction may be due to the incorporation of the bromide ion (from KBr), which also has a negative potential in solution, into the growing ice phase in place of incorporation of the chloride ion which is excluded from the ice phase.²³ The production of BrCl might thereby be reduced leading to less Br₂Cl⁻ product. Interhalide ions were still formed, as expected, because a fraction of the bromide concentration will remain in the unfrozen micropocket. The incorporation of the chloride ion into the ice phase which lowers the concentration of the chloride ion in the unfrozen micropockets may also play a significant role in the chemistry by lowering the chloride to bromide ratio thus favoring the production of Br₂Cl⁻ over BrCl₂⁻.

As acids have previously been shown to play a significant role in the formation of interhalides,^{19,20,34} an investigation into the role of acidity on the formation of bromine chloride interhalides in water-ice was conducted. With regard to polar environmental acid levels, low pH values have been

reported in both the Arctic and Antarctic regions due to sulfur dioxide pollution, which produces sulfuric acid in frost flower aerosols. The pHs of these aerosols have been reported to take values between 1.5 and 2.5.³⁵ In the current study, the production of the Br₂Cl⁻ species was found to depend strongly on the concentration of acid with higher levels leading to higher concentrations of dibromochloride ions being formed in frozen solutions. The individual absorbances at 232 (BrCl/BrCl₂⁻) and 245 nm (Br₂Cl⁻) are shown in Figure S3 of the Supporting Information.

Figure 4 shows the pH-dependence of the freeze-induced formation of the dibromochloride interhalide. As can be seen

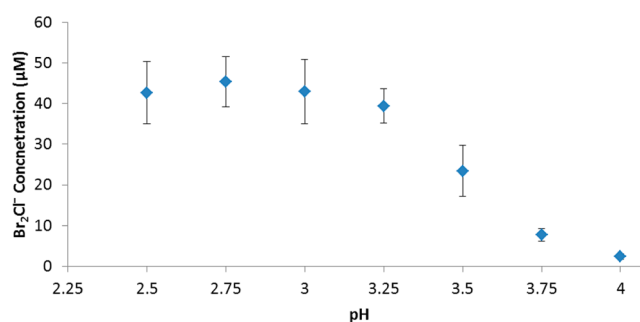
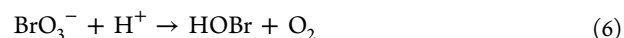


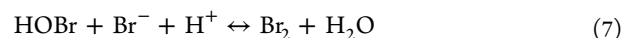
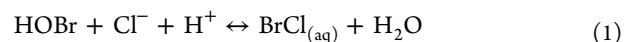
Figure 4. Dibromochloride concentration versus pH in frozen solutions of 0.57 M NaCl, 0.82 mM KBr, and 41 μM NaBrO₃.

the concentration of Br₂Cl⁻ formed drops rapidly between pH 3.25 and 4. Furthermore, no additional product formation was indicated from the spectra with pH < 3. The fact that no further formation of products at pH less than 3 is observed may be due to one or more of the reagents being fully consumed. As can be seen from Figure 4 the maximum concentration of Br₂Cl⁻ observed is approximately 42 μM, which is similar to that of initial bromate ions in the reaction flasks. This finding suggests that the concentration of bromate ions does limit the amount of dibromochloride ions formed. Additionally, when no acid is added to the system, no interhalide formation is observed in the frozen solutions.

Chemical Mechanisms of Interhalide Ion Formation in Water-Ice. The necessity for acidic conditions observed in the current set of experiments suggests that the initial step likely involves the protonation of the bromate ions in solution, which leads to the production of hypobromous acid and dissolved oxygen.



The hypobromous acid may subsequently react further with the acid and the chloride or bromide ions to form aqueous bromine or BrCl as described in reactions 1 and 7.



To explore the chemical mechanisms of the frozen systems further, a solution containing no bromate ion was frozen and then thawed. The UV spectrum of this solution was recorded and showed no absorption bands in the wavelength range 220–500 nm suggesting that no interhalide ion was formed. Therefore, it was apparent that both BrO₃⁻ and acid were required for the absorption peaks at 232–245 nm and 381–390 nm to appear after freezing. Hence, the evidence presented here

indicates that bromate ions and acid are necessary for interhalide ion formation by initially reacting to form hypobromous acid.

The concentration of bromate in solution affects the concentration of hypobromous acid produced and as such the effect of the initial bromate concentration on the production of the interhalide products was investigated. As can be seen in Figure 5 when the concentration of bromate is

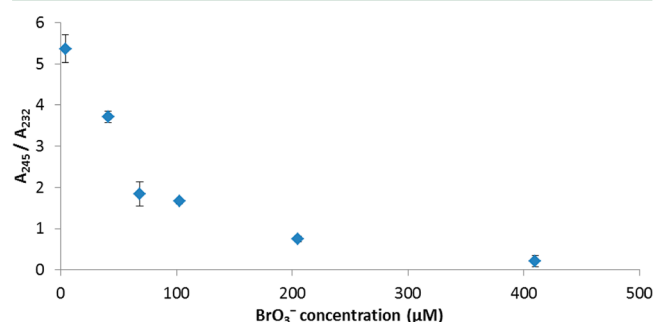


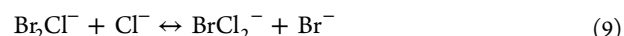
Figure 5. Ratio of absorbances for the 232 and 245 nm features vs bromate concentration in postfrozen solutions of composition, [Cl⁻] 0.57 M, [Br⁻] 0.82 mM, and pH 2.5.

decreased from 410 to 41 μM, the absorbance of the feature at 232 nm (BrCl/BrCl₂⁻) is reduced. Concurrently, the feature at 245 nm (Br₂Cl⁻) shows an absorbance increase. In addition, an absorption peak at 343 nm appears when the bromate concentration is >205 μM. This observation implies that the BrCl/BrCl₂⁻ interhalides are formed but only at a relatively high bromate ion concentration. As the bromate concentration is reduced toward 41 μM the absorbance at 343 nm (BrCl/BrCl₂⁻) is also reduced but other absorption bands begin to appear at 381 nm (Br₂Cl⁻). Therefore, it appears that decreasing the bromate concentration favors the formation of the more brominated interhalide. Lowering the concentration of added bromate ions from 41 to 4.1 μM reduced the concentration of Br₂Cl⁻ from approximately 4.14 × 10⁻⁵ M to 4.83 × 10⁻⁶ M, although it remained the dominant product. As the BrCl₂⁻ concentration was difficult to accurately quantify in the current study, due to the interference of several potential products at 232 nm, the ratios of the absorbances (A) measured at 232 and 245 nm were used to study any potential effect. The individual absorbance levels at 232 and 245 nm are shown in Figure S4 of the Supporting Information.

From Figure 5, it appears that as the concentration of bromate ion increases, the absorbance at 232 nm (BrCl/BrCl₂⁻) is favored over the absorbance at 245 nm (Br₂Cl⁻). This observation is in line with previous reports on the type of interhalide formed when high bromate concentrations are employed.^{12,34} However, the formation of the dibromochloride interhalide ion using relatively low bromate concentrations (μM) has not been reported before. The cause for this reaction pathway change after freezing is likely due to pathways that alter the ratio of halide ions in solution. This phenomenon has previously been noted when the freeze-concentration effect is operative.¹⁹ Hence, in the low-bromate concentration frozen solutions the following equilibria, shown as reactions 3 and 8, would be expected to become established.



Clearly, both the dibromochloride and the dichlorobromide interhalides may be formed through the intermediacy of BrCl. The system here is analogous to that found for the formation of I₂Br⁻ and IBr₂⁻ interhalide ions, when IBr acts as an intermediary in the resulting equilibrium processes.¹⁹ The summation of reactions 3 and 8 leads to reaction 8 below, which indicates the balance between the anions in solution.



Reaction 9 shows that if bromide ions are oxidized and removed from the system, the reaction favors the formation of the dichlorobromide interhalide. This process would be expected to occur when high concentrations of bromate ions are employed. Then HOBr is efficiently formed, and reaction 7 can occur by removing the bromide ion from the system through the oxidation of the bromide ion to bromine. This process in turn drives reaction 9 toward the formation of the dichlorobromide product.

As the dibromochloride ion appears to be the main interhalide ion formed at low bromate ion concentrations, it may be that bromide oxidation only occurs in the system at relatively high concentrations (>205 μM BrO₃⁻). Thus, at low bromate concentrations, bromide oxidation becomes less likely. This effect would lead to greater bromide concentrations being present in solution at low BrO₃⁻ concentration conditions and would again result in favored dibromochloride production through reaction 9.

To determine the effect of the bromide and chloride concentrations on interhalide ion formation the ratio between the chloride and bromide ions in solution was altered. Reaction 9 would predict that as the chloride concentration is reduced relative to bromide, dibromochloride formation will be favored and vice versa. The results are summarized in Figure 6. The individual absorbance levels at 232 and 245 nm are shown in Figure S5 of the Supporting Information.

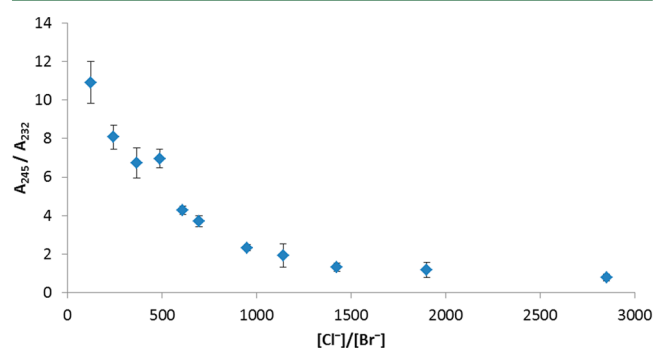


Figure 6. Comparison between the chloride to bromide ion concentration ratio and the ratio of the UV absorbances measured at 245 and 232 nm of composition pH 2.5 with a [BrO₃⁻] of 41 μM after freeze–thaw.

In Figure 6, it can be seen that as the [Cl⁻]/[Br⁻] ratio increases the A₂₄₅/A₂₃₂ ratio decreases. This finding suggests that as the concentration of chloride ions increases the formation of BrCl₂⁻/BrCl is favored over Br₂Cl⁻. This behavior is to be expected from consideration of reaction 9 whereby an increasing chloride ion concentration drives the reaction to the right and vice versa. Simply stated it is clear from Figure 6 that Cl⁻:Br⁻ concentration ratios found in Arctic or Antarctic environments would likely play a large role in the determination of any interhalides formed. In fact, in polar

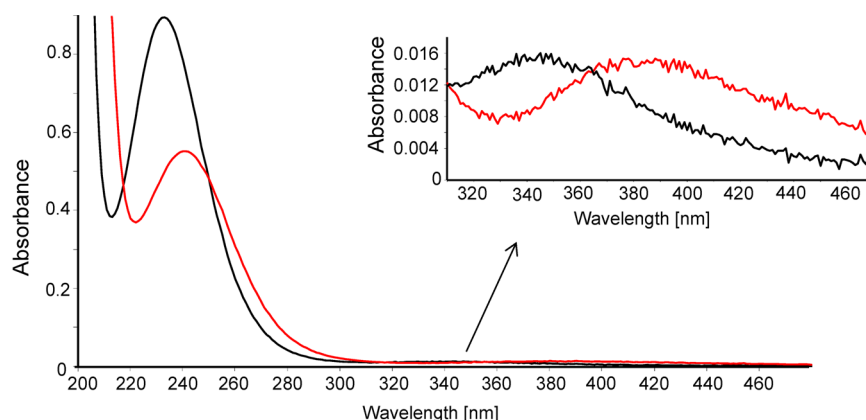


Figure 7. Comparison between UV spectra taken before and after the addition of bromide ions to mixture 2. Freeze–thaw solutions excluding the bromide ion (black line) and following addition of bromide ion (red line).

environments the ratio between the chloride and bromide ions has been reported to vary from 30 to 800.³⁶

Finally, experiments focused on determining whether any freezing reactions would occur in the absence of chloride or bromide ions were performed. These were initially conducted with the bromide ions excluded from solutions which were subsequently frozen. Upon analysis of the resulting UV spectra, as shown in Figure 7, absorption peaks at 232 and 343 nm (black line) characteristic of $\text{BrCl}/\text{BrCl}_2^-$ were identified as expected from reaction 1. Subsequently, bromide ions (0.82 mM) were added to these solutions and spectra taken immediately. A large reduction in absorbance at 232 nm was observed alongside a peak shift to 244 nm (red line). This behavior clearly indicates that any BrCl is reacting with Br^- ions to form Br_2Cl^- in line with reaction 3 and reaction 9.

Chloride ions were then excluded from solutions prior to freezing. Once frozen and thawed the resultant spectra showed peaks at 266 nm and ca. 390 nm as shown in Figure S6 of the Supporting Information. These results suggest that the reaction between acidified bromate and bromide ions forms both the tribromide ion and aqueous bromine. This reaction would be expected to occur by means of the following reaction pathway.³⁴



When chloride ions (0.57 M) were added to this solution following freezing and thawing, the absorption peak at 266 nm shifts to 244 nm but no change in the peak at 390 nm is observed. These spectra indicate that Br_2Cl^- ions are present in the solution and likely in the BrBrCl^- form. The addition of Cl^- to solutions containing aqueous tribromide ion and aqueous bromine therefore leads to the reaction described by reaction 4. Of course in this system the BrCl_2^- interhalide ion may be subsequently formed in solution through reaction 9. Indeed, it has been previously observed that trihalide ions may exist in equilibria with each other and McIndoe and Tuck³⁷ have shown, through the use of electrospray mass spectrometry that, when the chloride ion is added to solutions of tribromide ions, poly(inter)halide ions are formed that is, Br_2Cl^- , BrCl_2^- , and Cl_3^- . From the UV spectra obtained in the current experiments, it can be seen that there is evidence for Br_3^- , Br_2Cl^- , and BrCl_2^- ions all being formed in solution after freezing.

In aqueous solutions held at room temperature, previous studies have shown that the major product is the Cl_2Br^- trihalide ion when solutions of bromate, acid, bromide, and

chloride ions are left to equilibrate. In contrast, the results of the cryochemical experiments presented here suggest that the dibromochloride ion (BrBrCl^-) is the major product when solutions of bromate ($[\text{BrO}_3^-] < 210 \mu\text{M}$), acid, bromide, and chloride ions ($[\text{Cl}^-]/[\text{Br}^-] < 2000$) are frozen. Such a species would preferentially release bromine to the gas phase. Hence, the same halide starting materials form structurally different trihalide ions when frozen and these produce differing active halogens (BrCl and Br_2). This is a potentially important finding because Br_2 is photolyzed more readily and to longer wavelengths than BrCl and therefore the efficiency in forming products that can lead to ozone destruction in the atmosphere would be increased.^{11,38} The experiments conducted here are likely to be representative of polar aerosols/polar snowpack in terms of the pH likely to be encountered.

Results from the experiments found that temperature influenced the magnitude of product formation (decreasing temperature increased Br_2Cl^- formation), whereas the results also show that the freeze-concentration effect is a likely cause of the observed rate accelerations. In addition, the formation of the dibromochloride product was found to be especially effective when a negative potential was available in the ice. Both bromate ions and acid were required for the reactions to occur due to their role in the formation of hypobromous acid. Furthermore, both the acid concentration and the bromate ion concentration were found to influence the magnitude of the interhalide species formed. The concentration ratio of the chloride to bromide ions used in addition to the bromate concentration was shown to determine the nature of the interhalide product formed following freezing and thawing.

The atmospheric relevance of the reaction is clearly limited both by the necessity for high acidity levels and by the concentration of bromate ions utilized here. However, polar aerosols containing high levels of acidity have been identified,³⁵ which suggests that the freeze-induced acceleration of interhalide formation observed in the laboratory may occur in polar aerosols. In addition, polar snowpack pH levels have been reported to be in the region of 4.5–5.5 thereby suggesting that under the appropriate conditions the formation of interhalides may occur.^{39,40} As the production of the interhalides also depends on the bromate/hypobromous acid concentration, it would be useful to have accurate measurements of the bromate and hypobromous acid species in the polar regions to fully establish the potential atmospheric significance of this work. The importance of the Br_2Cl^- ion to the atmosphere is that

once formed the dibromochloride ions can decompose to either aqueous Br₂ or BrCl. These products can subsequently diffuse from the aerosols/snowpack to the gas phase releasing bromine and chlorine species to the atmosphere, which may subsequently contribute to ozone depletion.

■ ASSOCIATED CONTENT

■ Supporting Information

Individual absorbance following spectral deconvolution of the raw spectrum at 232 and 245 nm, raw spectra of solutions of differing compositions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: j.sodeau@ucc.ie.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to thank Science Foundation Ireland (SFI/08/RFP/CHE1010) for the funding this research.

■ REFERENCES

- (1) Steffen, A.; Douglas, T.; Amyot, M.; Ariya, P.; Aspmo, K.; Berg, T.; Bottenheim, J.; Brooks, S.; Cobbett, F.; Dastoor, A. A synthesis of atmospheric mercury depletion event chemistry in the atmosphere and snow. *Atmos. Chem. Phys.* **2008**, *8* (6), 1482.
- (2) Bottenheim, J. W.; Barrie, L. A.; Atlas, E.; Heidt, L. E.; Niki, H.; Rasmussen, R. A.; Shepson, P. B. Depletion of lower tropospheric ozone during arctic spring: The polar sunrise experiment 1988. *J. Geophys. Res.* **1990**, *95* (D11), 18555–18568.
- (3) Finlayson-Pitts, B. The tropospheric chemistry of sea salt: A molecular-level view of the chemistry of NaCl and NaBr. *Chem. Rev.* **2003**, *103* (12), 4801–4822.
- (4) Simpson, W.; Von Glasow, R.; Riedel, K.; Anderson, P.; Ariya, P.; Bottenheim, J.; Burrows, J.; Carpenter, L.; Frieß, U.; Goodsite, M. Halogens and their role in polar boundary-layer ozone depletion. *Atmos. Chem. Phys. Discuss* **2007**, *7* (2), 4285–4403.
- (5) Barrie, L.; Bottenheim, J.; Schnell, R.; Crutzen, P.; Rasmussen, R. Ozone destruction and photochemical reactions at polar sunrise in the lower Arctic atmosphere. *Nature* **1988**, *334*, 138–141.
- (6) Holmes, C.; Jacob, D. J.; Yang, X. Global lifetime of elemental mercury against oxidation by atomic bromine in the free troposphere. *Geophys. Res. Lett.* **2006**, *33*, L20808.
- (7) O'Connor, R.; O'Sullivan, D.; Sodeau, J. R. Dark oxidation of dissolved gaseous mercury in polar ice mimics. *Environ. Sci. Technol.* **2012**, *46* (9), 4829–4836.
- (8) Neuman, J.; Nowak, J.; Huey, L.; Burkholder, J.; Dibb, J.; Holloway, J.; Liao, J.; Peischl, J.; Roberts, J.; Ryerson, T. Bromine measurements in ozone depleted air over the Arctic Ocean. *Atmos. Chem. Phys.* **2010**, *10*, 6503–6514.
- (9) Liao, J.; Huey, L. G.; Tanner, D. J.; Flocke, F. M.; Orlando, J. J.; Neuman, J. A.; Nowak, J. B.; Weinheimer, A. J.; Hall, S. R.; Smith, J. N.; Fried, A.; Staebler, R. M.; Wang, Y.; Koo, J. H.; Cantrell, C. A.; Weibring, P.; Walega, J.; Knapp, D. J.; Shepson, P. B.; Stephens, C. R. Observations of inorganic bromine (HOBr, BrO, and Br₂) speciation at Barrow, Alaska, in spring 2009. *J. Geophys. Res.* **2012**, *117*, D00R16.
- (10) Vogt, R.; Crutzen, P. J.; Sander, R. A mechanism for halogen release from sea-salt aerosol in the remote marine boundary layer. *Nature* **1996**, *383*, 327–330.
- (11) Foster, K. L.; Plastring, R. A.; Bottenheim, J. W.; Shepson, P. B.; Finlayson-Pitts, B. J.; Spicer, C. W. The role of Br₂ and BrCl in surface ozone destruction at polar sunrise. *Science* **2001**, *291* (5503), 471–474.
- (12) Liu, Q.; Margerum, D. W. Equilibrium and kinetics of bromine chloride hydrolysis. *Environ. Sci. Technol.* **2001**, *35* (6), 1127–1133.
- (13) Bartlett, W. P.; Margerum, D. W. Temperature dependencies of the Henry's law constant and the aqueous phase dissociation constant of bromine chloride. *Environ. Sci. Technol.* **1999**, *33* (19), 3410–3414.
- (14) Burger, K.; Schulek, E. The use of bromine chloride in analytical chemistry: Determination of unsaturated aldehydes. *Talanta* **1960**, *7* (1–2), 46–50.
- (15) Takenaka, N.; Daimon, T.; Ueda, A.; Sato, K.; Kitano, M.; Bandow, H.; Maeda, Y. Fast oxidation reaction of nitrite by dissolved oxygen in the freezing process in the tropospheric aqueous phase. *J. Atmos. Chem.* **1998**, *29* (2), 135–150.
- (16) Takenaka, N.; Furuya, S.; Sato, K.; Bandow, H.; Maeda, Y.; Furukawa, Y. Rapid reaction of sulfide with hydrogen peroxide and formation of different final products by freezing compared to those in solution. *Int. J. Chem. Kinet.* **2003**, *35* (5), 198–205.
- (17) Finnegan, W. G.; Pitter, R. L.; Hinsvark, B. A. Redox reactions in growing single ice crystals: A mechanistic interpretation of experimental results. *J. Colloid Interface Sci.* **2001**, *242* (2), 373–377.
- (18) Betterton, E.; Anderson, D. Autooxidation of N (III), S (IV), and other species in frozen solution – a possible pathway for enhanced chemical transformation in freezing systems. *J. Atmos. Chem.* **2001**, *40* (2), 171–189.
- (19) O'Sullivan, D.; Sodeau, J. Freeze-induced reactions: Formation of iodine-bromine interhalogen species from aqueous halide ion solutions. *J. Phys. Chem. A* **2010**, *114*, 348.
- (20) O'Driscoll, P.; Lang, K.; Minogue, N.; Sodeau, J. Freezing halide ion solutions and the release of interhalogens to the atmosphere. *J. Phys. Chem. A* **2006**, *110* (14), 4615–4618.
- (21) Pincock, R. Reactions in frozen systems. *Acc. Chem. Res.* **1969**, *2* (4), 97–103.
- (22) Oldridge, N. W.; Abbatt, J. P. D. Formation of gas-phase bromine from interaction of ozone with frozen and liquid NaCl/NaBr solutions: Quantitative separation of surficial chemistry from bulk-phase reaction. *J. Phys. Chem. A* **2011**, *115* (12), 2590–2598.
- (23) Cobb, A. W.; Gross, G. W. Interfacial electrical effects observed during the freezing of dilute electrolytes in water. *J. Electrochem. Soc.* **1969**, *116*, 796.
- (24) Workman, E. J.; Reynolds, S. E. Electrical phenomena occurring during the freezing of dilute aqueous solutions and their possible relation to thunderstorm electricity. *Phys. Rev.* **1950**, *78*, 254–9.
- (25) Von Gunten, U.; Hoigné, J. Bromate formation during ozonation of bromide-containing waters: Interaction of ozone and hydroxyl radical reactions. *Environ. Sci. Technol.* **1994**, *28* (7), 1234–1242.
- (26) Liu, Q.; Schurter, L. M.; Muller, C. E.; Aloisio, S.; Joseph, S.; Margerum, D. W. Kinetics and mechanisms of aqueous ozone reactions with bromide, sulfite, hydrogen sulfite, iodide, and nitrite ions. *Inorg. Chem.* **2001**, *40* (17), 4436–4442.
- (27) Iraci, L.; Michelsen, R.; Ashbourn, S.; Rammer, T.; Golden, D. Uptake of hypobromous acid (HOBr) by aqueous sulfuric acid solutions: low-temperature solubility and reaction. *Atmos. Chem. Phys.* **2005**, *5* (6), 1577–1587.
- (28) Takenaka, N.; Ueda, A.; Daimon, T.; Bandow, H.; Dohmaru, T.; Maeda, Y. Acceleration mechanism of chemical reaction by freezing: The reaction of nitrous acid with dissolved oxygen. *J. Phys. Chem.* **1996**, *100* (32), 13874–13884.
- (29) Ogawa, Y.; Takahashi, O.; Kikuchi, O. Ab initio MO study of structure and stability of heteronuclear trihalide anions X₂Y[−] (X, Y = Cl, Br, or I) in the gas phase and in solution. *J. Mol. Struct. THEOCHEM* **1998**, *429*, 187–196.
- (30) Takenaka, N.; Bandow, H. Chemical kinetics of reactions in the unfrozen solution of ice. *J. Phys. Chem. A* **2007**, *111* (36), 8780–8786.
- (31) Wolff, E.; Mulvaney, R.; Oates, K. The location of impurities in Antarctic ice. *Ann. Glaciol* **1988**, *11*, 194–197.
- (32) Koop, T.; Kapilashrami, A.; Molina, L. T.; Molina, M. J. Phase transitions of sea-salt/water mixtures at low temperatures: Implications for ozone chemistry in the polar marine boundary layer. *J. Geophys. Res.* **2000**, *105*, (D21), 26393–26402.

- (33) Workman, E. J.; Reynolds, S. Electrical phenomena occurring during the freezing of dilute aqueous solutions and their possible relationship to thunderstorm electricity. *Phys. Rev.* **1950**, 78 (3), 254.
- (34) Wang, T. X.; Kelley, M. D.; Cooper, J. N.; Beckwith, R. C.; Margerum, D. W. Equilibrium, kinetic, and UV-spectral characteristics of aqueous bromine chloride, bromine, and chlorine species. *Inorg. Chem.* **1994**, 33 (25), 5872–5878.
- (35) Piot, M.; von Glasow, R. The potential importance of frost flowers, recycling on snow, and open leads for ozone depletion events. *Atmos. Chem. Phys. Discuss.* **2007**, 7 (2), 4521–4595.
- (36) Toom-Sauntry, D.; Barrie, L. Chemical composition of snowfall in the high Arctic: 1990–1994. *Atmos. Environ.* **2002**, 36 (15–16), 2683–2693.
- (37) Scott McIndoe, J.; Tuck, D. G. Studies of polyhalide ions in aqueous and non-aqueous solution by electrospray mass spectrometry. *Dalton Trans.* **2003**, 2, 244–248.
- (38) Hubinger, S.; Nee, J. Absorption spectra of Cl_2 , Br_2 and BrCl between 190 and 600 nm. *J. Photochem. Photobiol., A* **1995**, 86 (1), 1–7.
- (39) Douglas, T. A.; Sturm, M. Arctic haze, mercury and the chemical composition of snow across northwestern Alaska. *Atmos. Environ.* **2004**, 38 (6), 805–820.
- (40) DeFelice, T. P. Chemical composition of fresh snowfalls at Palmer Station, Antarctica. *Atmos. Environ.* **1998**, 33 (1), 155–161.