Experimental Verification of Gas Phase Bromine Enrichment in Reactions of HOBr with Sea Salt Doped Ice Surfaces

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Significant gas phase bromine enrichment is experimentally verified on flowing gaseous HOBr over ice surfaces doped with sodium halides of sea salt composition. It is argued that formation of Br_2Cl^- in the condensed phase followed by its dissociation with release of Br_2 into the gas phase accounts for this phenomenon.

Introduction

Episodic destruction of boundary layer ozone from normal (~40 ppb) to unmeasurable low (<1 ppb) levels have repeatedly been observed in the Arctic shortly after polar sun rise [1-5]. The observations were strongly correlated with high levels of originally not identified bromine compounds which have been collected on cellulose filters [2]. Since the observed near-total ozone depletion occurred too fast to be interpreted on the basis of standard gas phase chemistry, McConnell et al. [6] postulated a photoinduced heterogeneous conversion pathway for Br⁻ as discussed in the photochemistry of environmental aquatic systems [7]. A continuous recycling of inorganic bromine between aerosols and the gas phase was assumed to maintain sufficiently high Br₂ levels in the atmosphere, which upon photolysis could account for the observed ozone depletion. Fan and Jacobs [8] modelled a mechanism based on known aqueous phase chemistry [9] in which a heterogeneous back conversion was assumed on sulfuric acid aerosols of HBr and HOBr to Br and BrO. BrO mixing ratios of 4 to 17 ppt have been measured for the first time by Hausmann and Platt [10] using differential optical absorption spectroscopy. A simple scenario involving a combination of advection, atmospheric dispersion and BrO-catalysed chemical ozone destruction was described by these authors which could explain the observed ozone losses.

Recently three new model studies have been published, which dealt with possible reasons for such an apparently preferred mechanism of ozone depletion based on bromine chemistry. Mozurkewich [11] has speculated on initial bromine release from sea salt particles by free radical reactions involving Caro's acid, followed by possible autocatalytic cycles to release bromine from sea salt. Mozurkewich has pointed out that these mechanisms will not be effective as source for photochemically active Cl. Vogt et al. [12] have presented a mechanism for halogen release from sea salt aerosols in the remote marine boundary layer (MBL). These authors have refuted Mozurkewich's proposals for reactive bromine production in the pristine MBL or in the Arctic. Instead they proposed a more general halogen chemistry mechanism operative in the liquid and the gas phase. The crucial statements in their contribution are related to the high abundance of Cl^- in sea water and thus also in the nascent sea salt aerosol, leading to the preferred liquid phase ionic reaction

$$HOBr_{aq} + Cl^{-} + H^{+} \rightarrow BrCl_{aq} + H_{2}O .$$
 (1)

Finally Tang and McConnell [13] reported a mechanism for the release of bromine during polar sunrise from snow pack on ice covering the Arctic ocean. They do not apply reaction (1) but base their discussion on the diffusion of HBr into an acidified aerosol forming Br^- which can react with HOBr_{aq} according to (2)

$$HOBr_{aq} + Br^{-} + H^{+} \rightarrow Br_{2(aq)} + H_2O .$$
 (2)

The $Br_{2(aq)}$ can subsequently evolve to yield $Br_{2(g)}$. In this mechanism the production of Br_2 is limited by the uptake of either $HOBr_{(g)}$ or $HBr_{(g)}$ by the aerosol.

Experimental evidence to support the proposed mechanisms and/or to elucidate the probability (γ) for reactions (1) and (2) are very scarce. Abbatt's report on the heterogeneous reactions of HOBr with HBr and with HCl on ice surfaces at 228 K [14] is the only investigation known. While the present authors fully agree with the basic results reported by Abbatt, we find that an important aspect of the reactions studied has remained unnoticed, i.e. the significant enrichment in Br_{2(g)} executing the heterogeneous process (1) on alkali halides of sea salt composition. This communication presents experimental evidence for efficient halogen release from alkali halide-doped ice surfaces through interaction with HOBr and reports on an observed gas phase bromine enrichment. The results are consistent with the model proposed by Vogt et al. [12].

Experimental

All experiments were carried out in a flow tube equipped with a sliding injector similar to those used in homogeneous gas kinetic studies [15, 16]. The flow tube was connected to a Bruker Reflectron time of flight mass spectrometer (TOF) via a differential pumping stage for molecular beam sampling. The TOF was equipped with an electron impact ion source. Using a fast data acquisition mode [17] we were able to acquire and to add complete spectra in the range 30 < mass/amu < 300 at a rate of 800 Hz in a Bruker B500 transient recorder. The reactor consisted of a jacketed flow tube of 23.8 mm inner diameter. Its temperature was controlled by pumping ethanol through the jacket. The temperature of the reactor was registered by thermocouples, which were attached to the outer tube surface. The sliding injector was a Pyrex glass tube of 8 mm outer diameter, which contained a teflon tube for the transport of the reactant HOBr. The teflon tube was surrounded by a heating wire which allowed moderate warming to prevent freezing in the injector or decomposition of the reactant (see below). Carrier gas flow velocities were up to $8 \,\mathrm{ms}^{-1}$ at total pressures ranging from routinely 5 up to 20 mbar. The flow system

could be disconnected from the mass spectrometer by a metal-free mechanical shutter. This device was located inside the differential pumping chamber of the MS. With the teflon seal open, gas from the flow system was sampled through a 0.4 mm Macor nozzle. The shutter could be operated at 5 Hz.

Ice coverages in the reactor tube were generated by spraying liquid water onto the cooled tube inner surface using a specially designed injector. Doped ice surfaces characteristic for sea salt aerosol were obtained by spray-freezing a solution of 30 g NaCl and 81 mg NaBr in 100 ml water onto the flow tube wall. The Br⁻ content of the analytical grade NaCl was < 0.005%. The conductivity of the demineralized water used was always $< 0.1 \,\mu \text{S} \cdot \text{cm}^{-1}$.

Aqueous solutions of HOBr were prepared in analogy to the method of Spiller and Dancer [18]. Further purification by destillation and acidification with 20 wt.% sulfuric acid resulted in stable, approx. 0.2 M solutions of HOBr. Gaseous HOBr samples for all experiments were obtained by bubbling He through the freshly prepared solutions kept at room temperature. The gas flow was passed through a cold trap at 0°C to decrease the water content. The Br₂O content of the gaseous HOBr samples never exceeded 2%. The amounts of Br₂ and HBr in the effluent were found to be less than 1%.

Results and Discussion

On passing HOBr samples slowly over sea salt-doped ice at T = 240 K the spectrum shown in Fig. 1 a was obtained. Virtually complete conversion of HOBr is noted which leads to the formation of BrCl and significant amounts of Br₂. Only traces of Cl₂ were formed. Fig. 1b shows the spectrum of an identical sample with $[HOBr] \sim 10^{13}$ molecule cm⁻³ after having been slowly transported over an undoped ice surface at the same temperature. The residence



MS analysis to demonstrate the complete conversion of gaseous HOBr into BrCl and Br₂ by transport over sea salt-doped ice at T = 240 K (a). The spectrum of HOBr transported at the same temperature over undoped ice is given in (b). Ion signals in the range 174 - 178 amu are due to Br_2O^+ and to its fragments Br_2^+ (158 – 162 amu) together with BrO⁺ (95 and 97 amu) formed in the cold tube according to (3). (c) MS background

time of HOBr in the ice-covered tube was roughly 1 s. From the analysis of samples kept at T = 270 K it became apparent that ionizing our HOBr samples resulted in this mass range in ion signals practically only due to the parent masses 96 and 98 amu. The ion signals at 174 - 178, 158-162 and 95, 97 amu in Fig. 1b are due to Br_2O^+ , accompanied by its fragments Br_2^+ and BrO^+ , respectively, which is formed at the cold surface via the equilibrium (3).

$$2HOBr \neq Br_2O + H_2O \tag{3}$$

Measured first order HOBr losses on walls covered with undoped ice or with ice doped by NaBr are given in Fig. 2. The small HOBr loss on undoped ice is related to Br₂O formation according to (3), the strong losses on the doped ice surfaces are assigned to process (2). Evaluated surface reaction probabilities y from these runs and from investigations using other dopants are compiled in Table 1. The increase in γ with [HBr] is taken as evidence that protonated HOBr is the reactant. Similar experiments have also been carried out with HOCl and shall be presented elsewhere [18]. It is apparent from these kinetic investigations that γ for HOBr on NaBr-doped ice is only a factor ~ 3 larger compared to NaCl-doped ice. The reaction probability on ice doped with





First order decays of HOBr on doped ice surfaces (\bigcirc , \Box , \triangle) as function of injector position. On undoped ice surfaces only small HOBr losses are found (\Diamond) and simultaneously formation of Br₂O was observed

Table 1 Determination^a) of reaction probabilities y at 230 K < T < 240 K

Dopant	$[HOBr]_0$ 10 ¹³ molecule cm ⁻³	γ
30 wt.% NaCl	0.6-1.3	$(1.24 \pm 0.47) \cdot 10^{-3}$
30 wt.% NaBr	0.7 - 1.2	$(3.27 \pm 0.48) \cdot 10^{-3}$
30 wt.% NaCl with		
0.08 wt.% NaBr	0.9-1.3	$(1.42 \pm 0.17) \cdot 10^{-3}$
(1 < HBr < 30) wt. %	0.7 - 1.2	< 0.15

^a) Each determination was carried out with an individually prepared fresh ice cover. The y values reported are the average out of at least five determinations

NaCl/NaBr mixtures, with a composition very close to natural sea salt, is within experimental uncertainty the same as on analytical grade NaCl. Our γ values on HBr-doped ice are in acceptable agreement with data reported by Abbatt [14]. However, the detailed product analysis, in which HOBr consumption and BrCl as well as Br₂ formation were quantified, revealed that on ice doped with alkali halides of nearly sea salt composition BrCl is formed with $(42 \pm 10)\%$ and Br₂ with $(48 \pm 9)\%$ probability per HOBr molecule consumed, i.e. that Br₂ generation was enhanced by more than a factor of 500 as compared to the stoichiometry of the dopant. Identical results were obtained with different, individually prepared doped ice covers.

Although a small enrichment in the aerosol surface due to the difference in NaCl or NaBr solubility in water appears quite acceptable, it can be excluded that [Br⁻] is enriched in the surface to an extent to explain this increase. It is argued that BrCl is the dominant initial product in the interaction of HOBr with the doped ice surface. Initial formation of Br₂ via (2) will occur only according to the ratio $[Br^-]/[Cl^-] \sim 1.4 \cdot 10^{-3}$ in sea salt and shall be neglected here. It has been reported [19-21] that halogens and interhalogen compounds react diffusion controlled with halide ions in aqueous media. For the reaction of $BrCl_{aq}$ with Br⁻ a rate constant $k(6) > 10^8 M^{-1} s^{-1}$ has been derived [22]. Thus with halide ions being present in excess, the equilibria (5) – (7) will rapidly be established in the condensed phase:

$$BrCl_{aq} + Cl^{-} \Rightarrow BrCl_{2}^{-};$$

$$K_{5} = 6.0 \pm 0.3 \text{ M}^{-1} \quad [22] \qquad (5)$$

$$\operatorname{BrCl}_{\operatorname{aq}} + \operatorname{Br}^{-} \rightleftharpoons \operatorname{Br}_{2}\operatorname{Cl}^{-};$$

 $K_{6} = (1.8 \pm 0.2) \cdot 10^{4} \operatorname{M}^{-1} [22]$ (6)

$$Br_2Cl^- \Rightarrow Br_{2(aq)} + Cl^- ;$$

$$K_7 = 0.8 \pm 0.2 M [22]$$
(7)

It is to be noted that formation of Br_2Cl^- is limited by the availability of $[Br^-]$.

It is suggested that the observed enhancement in Br_2 release is related to both the thermodynamics of trihalide ion formation, i.e. their equilibrium constants, and to the hydrolysis kinetics of $Br_{2(aq)}$ as compared to $BrCl_{aq}$. In contrast to (8) hydrolysis of $BrCl_{aq}$ is a very rapid process (9)

$$Br_{2(aq)} + H_2O \rightarrow HOBr_{aq} + H^+ + Br^-;$$

 $k = 37 \text{ s}^{-1}$ [22] (8)

$$BrCl_{aq} + H_2O \rightarrow HOBr_{aq} + H^+ + Cl^-$$
;
 $k > 2 \cdot 10^5 \text{ s}^{-1}$ [22] (9)

Thus hydrolysis will drastically reduce the probability of $BrCl_{aq}$ to escape into the gas phase and leads to the enrichement in $Br_{2(g)}$. The observations require that a liquid film exists on the aerosol particles.

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