

BrCl production in NaBr/NaCl/HNO₃/O₃ solutions representative of sea-salt aerosols in the marine boundary layer

R. S. Disselkamp, E. G. Chapman, and W. R. Barchet

Atmospheric Sciences & Global Change Resources, Pacific Northwest National Laboratory, Richland, Washington

S. D. Colson

Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington

C. D. Howd

Department of Chemistry, University of Michigan at Flint, Flint, Michigan

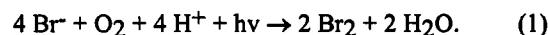
Abstract. Atomic bromine and chlorine liberated from sea-salt aerosol is thought to play an important role in chemistry of the marine boundary layer. Despite numerous modeling studies, no prior experimental investigations of the oxidation of halide species contained in simulated, or actual, sea-salt solutions have been performed. We present laboratory data that examines chemistry in NaBr/NaCl/HNO₃/O₃ solutions at 290 K. Ozonation experiments were performed by flowing ozone in air through a nitric acid/salt solution and monitoring pH with time using an ion-sensitive electrode. The rate of oxidation was observed to be first order in ozone concentration and to have a non-first order bromide concentration dependence. Ion chromatography was used to measure both bromide disappearance as well as oxidation products formed during the course of the reactions studied. Our measurements of the oxidation rate versus ion concentration indicate that the high ionic strength present in sea-salt aerosol will possess unique kinetics different from dilute solution behavior. In addition, our results are consistent with the reaction sequence $O_3 + H^+ + Br^- \rightarrow O_2 + HOBr$ and $HOBr + Cl^- + H^+ \rightarrow BrCl + H_2O$. These observations support the HOBr mediated Cl⁻ oxidation process proposed previously (Vogt et al., 1996).

Introduction

The oxidation of bromide and chloride in sea-salt aerosol is thought to be a source of gas-phase halogen-containing compounds in the marine boundary layer (MBL) and near coastal regions. These halogen compounds readily photolyze to yield atomic bromine and chlorine and have been implicated in episodes of Arctic ozone loss [Barrie et al., 1988; McConnell et al., 1992; Finlayson-Pitts and Pitts, 1997] and hydrocarbon oxidation [Jobson et al., 1994; Singh et al., 1996], respectively. Several field measurements have demonstrated the existence of oxidized forms of halogens in the MBL. In one technique, Cl₂ was observed directly at a North American ground site using atmospheric pressure chemical ionization mass spectroscopy (CIMS) [Spicer et al., 1998]. In a second

study, an alkaline mist chamber titration technique was used at a Florida coastal site to trap oxidized chlorine compounds (i.e., Cl₂, BrCl, ClNO₂, etc.) in solution from which concentrations ranging from <13 to 127 p.p.t. were determined [Keene et al., 1993; Pszenny et al., 1993]. A third study utilized field measurements of hydrocarbon concentrations together with a kinetic model of hydrocarbon oxidation to infer that atomic chlorine, at times, was the primary oxidant in the MBL and near coastal regions [Jobson et al., 1994]. These measurements implicate the existence of a halide oxidation pathway in the MBL and near coastal regions, possibly involving ozone and nitric acid.

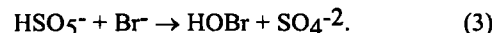
A variety of reactions have been proposed to account for the existence of gas-phase halogen-containing compounds. All begin with the aqueous phase oxidation of halide species contained within deliquescent sea-salt aerosols. Duce et al. [1966] and McConnell et al. [1992] proposed the formation of Br₂ in the presence of sunlight, oxygen, and sea-salt via the reaction



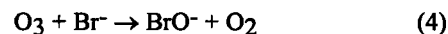
Fan and Jacob [1992] proposed a bromide oxidation reaction in which HOBr was postulated to be an important intermediate species



In their mechanism the origin of HOBr was unclear. In subsequent work Mozurkewich [1995] and Chameides and Stelson [1992] proposed a heterogeneous mechanism of HOBr production by the reaction of Caro's acid with bromide,



In the atmosphere, this rate of HOBr production was shown to greatly exceed the ozone mediated rate [Vogt et al., 1996] given by



Experiments have recently been performed by Hirokawa et al. [1998] that have demonstrated the formation of Br₂, consistent with reactions (2), (4), and (5) above. In their

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experiments, NaBr(s) in a Knudsen cell was exposed to O₃ and H₂O vapors and Br₂ was detected by mass spectroscopy. In an attempt to explain the observed depletion of chloride in sea-salt aerosol [Murphy *et al.*, 1997], Vogt *et al.* [1996] proposed the HOBr oxidation of chloride,



They argued that the high Cl⁻/Br⁻ molar ratio of sea-water of ~700 (i.e., high Cl⁻ activity) enables reaction (5) to be thermodynamically (and kinetically) more favored than reaction (2).

Although rate constants for bromide oxidation, namely reactions (4)-(6), have been measured previously [Haag and Hoigne, 1983; Beckwith *et al.*, 1996], the effect of high ionic strength on reaction rate has not been investigated. Since atmospheric sea-salt aerosol in the marine boundary layer under ambient conditions will possess an ionic strength greater than unity (see below), this is a potential cause of modeling error. We present here experimental evidence of a non-linear dependence of the reaction rate on bromide ion concentration and data that supports the hypothesis of BrCl formation in aqueous solutions representative of deliquesced sea-salt aerosol.

Experimental Procedure and Results

Experiments were performed by flowing 0.75 SLPM of zero-grade air (78.4 mol.% N₂, 21.6 mol.% O₂, <0.5 ppm impurities) through an ozone generator (Hg pen-ray lamp photolysis, Ozone Engineering Inc.) and into a gas dispersion assembly modified to accept an ion sensitive electrode. All experiments were performed at 290±2 K. A volume of 100 ml was used for the nitric acid/salt solutions studied. Commercially available reagent-grade chemicals were used: HNO₃ (VWR) 70 wt.%; NaCl (Aldrich) 99.999 wt.%; and NaBr (Aldrich) 99 wt.%. Water treated by reverse-osmosis was used without further purification. Ozone reactant concentrations were measured by flowing the gas stream through a White cell (Infrared Analysis) having an optical pathlength of 60 cm interfaced to an FTIR spectrometer (Nicolet Magna-IR 560). In each experiment the temporal variation of H⁺ (ion-sensitive electrode for pH) and Br⁻ (ion chromatographic technique) was measured over a period of about 80 minutes.

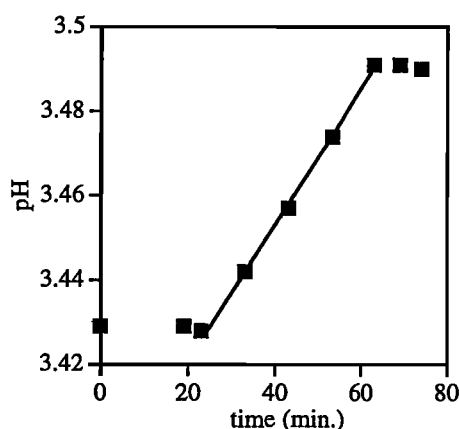


Figure 1. The variation of pH with time is shown for a 200 ppm NaBr, pH 3.5, solution. Zero air at 0.75 SLPM was flowed through the solution during the entire experiment. Initially the pH is constant at 3.43. Between $t=24$ min. and $t=64$ min. 15 ppm of ozone was added to the zero-air stream and the pH increased linearly with time. At 64 min. the ozone source was turned off and the pH again remained constant.

Figure 1 illustrates raw data representative of the pH experiments performed here to extract the total oxidation rate. Between 0-24 min. the pH electrode (Ross combination electrode model 8102) yielded a constant value of 3.43 while zero-air was sent through solution. At 24 min. ozone was introduced into the zero-air gas stream and acid concentration decreased with time. This increase in solution pH can be attributed to ozone initiated oxidation in solution. At 60 min. the ozone source was switched off and the pH maintained a constant value of 3.49. During the course of each experiment to extract an oxidation rate, only small changes in the aqueous halide and hydronium ion concentrations were allowed to occur.

To identify the species being oxidized, experiments were performed with and without NaCl and NaBr salts. Ozone initiated oxidation, resulting in pH change such as that shown in Figure 1, only occurred with bromide present, irrespective of whether chloride was contained in solution. Experiments confirmed the inability of ozone to oxidize chloride in aqueous solution [Latimer, 1952]. Furthermore, to examine whether ozone was saturated in solution, or whether its uptake into solution was transport limited, we performed experiments as a function of gas flow rate through solution at a constant ozone partial pressure. Our observation of identical kinetics independent of flow rate indicates that ozone was saturated in solution.

It is worthwhile to examine one additional cause of a change in solution pH with time, aside from chemistry, which is the preferential vaporization of either nitric acid or water from solution due to the flow of dry zero air. At saturation, water and nitric acid vapor pressures at 298 K are 3.1×10^{-2} and 3.7×10^{-15} atm, respectively [Carshaw *et al.*, 1995]. If 0.75 SLPM of dry air flows through the solution for 200 min. and the effluent gas is saturated with respect to these vapors, then 3.7 gm of water and a negligible amount of nitric acid will be depleted from the solution. Hence after 200 min. of air flow, the pH of an initial 100 gm (ml) sample with a pH of 3.500 will achieve a final value of 3.484. Since the rate of pH increase due to chemistry in our experiments is much greater than the pH decrease due to water vaporization, humidification of the effluent gas stream does not make an important contribution to the pH changes reported here. This was confirmed by experiments that revealed only a small change in solution pH (<0.01) on the time scale of our experiments when no ozone was introduced into the zero air gas stream.

The results of many kinetic experiments are summarized in Figures 2 and 3. Figure 2 shows the rate of hydronium ion consumption divided by the ozone partial pressure, $d\text{H}^+/dt \cdot 1/p(\text{O}_3)$, versus Br⁻ concentration for 0.0 and 2.0 M NaCl solutions. The solid circles and triangles for the 0.0 M NaCl solutions represent ozone partial pressures of 1.5×10^{-5} and 3.2×10^{-5} atm, respectively. Since the data lie along a common curve the reaction is first order with respect to ozone. A non-linear dependence of the reaction rate with bromide concentration is seen. At small bromide concentration ($<4.0 \times 10^{-4}$ M) we observed a linear dependence of the reaction rate with bromide concentration, yielding a reaction rate constant of $130 \text{ M}^{-1} \text{ s}^{-1}$ for $\text{Br}^- + \text{O}_3 \rightarrow \text{BrO}^- + \text{O}_2$. This value compares favorably to that of $160 \text{ M}^{-1} \text{ s}^{-1}$ obtained by Haag and Hoigne [1983] previously, where bromide concentration was varied from 5.0×10^{-5} to 1.0×10^{-3} M. The upper curve, illustrated by open squares, corresponds to 2.0 M NaCl solutions. An enhancement in the reaction rate due to the presence of chloride is clearly seen. This increase in oxidation rate may arise from an alternative reaction pathway afforded by the presence of chloride in solution (see

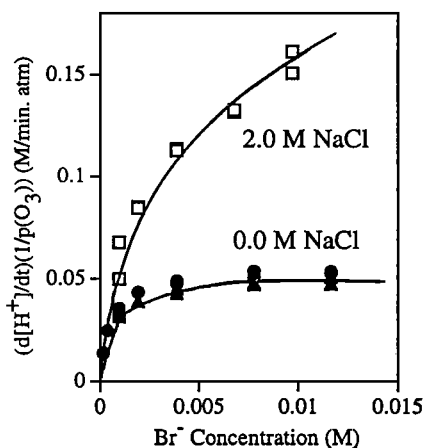


Figure 2. The rate of hydronium ion consumption normalized to ozone partial pressure, as a function of bromide ion concentration, is shown for pH 3.5 solutions. For the 0.0 M NaCl experiments, the solid circles and triangles represent experiments with ozone concentrations of 15 and 32 ppm, respectively. The 2.0 M NaCl experiments, denoted by open squares, were performed using 32 ppm ozone. The solid curves are an interpolated best fit of the data.

reaction (6)). In both sets of data the cause of the non-linear dependence of the reaction rate on bromide concentration is not known, but may be due to ion solvation effects.

To more realistically simulate the chemistry of deliquesced sea-salt aerosols, we performed kinetic experiments having a Cl⁻:Br⁻ molar ratio of 700, which is representative of seawater [Vogt *et al.*, 1996]. Figure 3 presents the results of experiments in which the net rate of oxidation divided by ozone partial pressure is plotted against NaCl salt molarity. A linear fit to the data is given by the solid line. It is seen that a four-fold increase in salt concentration, such as that which would occur in an aerosol in an air parcel undergoing a change in relative humidity from 98% to 85% [Tang *et al.*, 1986], results in approximately a four-fold increase in oxidation rate. Based on our discussion above there is no reason to expect a linear relationship for this data. It is important to note that for relative humidities typically encountered in the marine boundary layer of <98% corresponds to a bromide concentration of >1.4 × 10⁻³ M, hence according to Figure 2 non-linear oxidation rate behavior may occur.

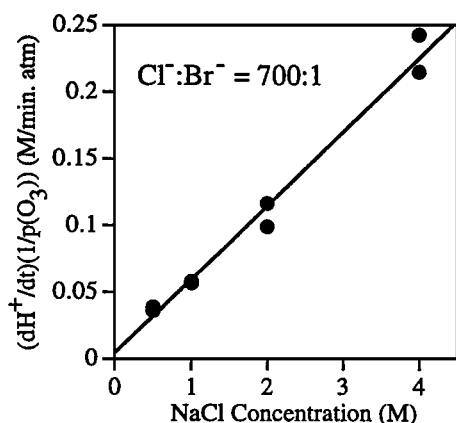


Figure 3. The rate of hydronium ion consumption normalized to ozone partial pressure, as a function of NaCl concentration, is shown for pH 4.0 solutions. The Cl⁻:Br⁻ molar ratio was maintained at 700:1 in these experiments.

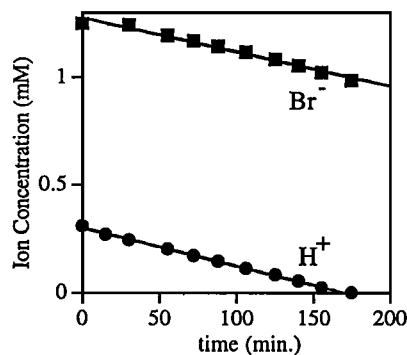


Figure 4. The concentration of hydronium and bromide ions as a function of time is shown for a 100 ppm NaBr, pH 3.0, solution. The nearly identical ion depletion rates indicate a 1:1 chemical reaction stoichiometry exists between H⁺ and Br⁻.

The oxidation rate results presented thus far supply us with little mechanistic information about the reaction process. In order to determine the species being oxidized in the mixed salt experiments, as well as the oxidation products formed, we employed ion chromatography to study the reaction process. Analyses were performed using a Dionex model 4000I ion chromatograph employing suppressed conductivity detection. Separation and quantitation of target analytes (Br⁻, BrO₃⁻, Cl⁻, ClO₂⁻, ClO₃⁻, and NO₃⁻ ions) were accomplished using a Dionex AS9HC separator column with 9 mM Na₂CO₃ eluent pumped at 1.5 mL/min. Figures 4 and 5 show plots representative of hydronium and bromide concentration versus time for 0.0 M and 2.0 M NaCl solutions, respectively. Figure 4 reveals nearly identical H⁺ and Br⁻ ion depletion rates of -1.7 × 10⁻³ and -1.6 × 10⁻³ mM/min., respectively. Therefore, a 1:1 stoichiometric reaction between H⁺ and Br⁻ has occurred. This is not the situation for the mixed salt experiment. Figure 5 shows H⁺ and Br⁻ depletion rates of -8.0 × 10⁻³ and -4.1 × 10⁻³ mM/min., respectively, with 2.0 M NaCl present in solution. Due to the large excess of chloride in the 2.0 M NaCl experiment, its ion disappearance rate could not be detected. In these experiments, only half of the oxidation arises from bromide consumption with the balance

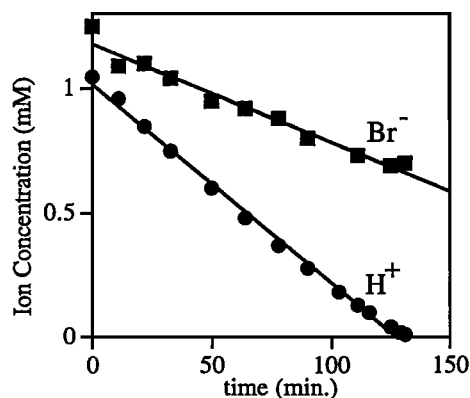


Figure 5. The concentration of hydronium and bromide ions as a function of time is shown for a 100 ppm NaBr/pH 3.0/2.0 M NaCl solution. The ion disappearance rates of -8.0 × 10⁻³ mM/min. for hydronium, and -4.1 × 10⁻³ mM/min. for bromide, reveal the net rate of oxidation is twice as great in the presence of chloride as that for bromide oxidation alone. This result suggests that the oxidation process entails a Cl⁻:Br⁻ molar ratio of 1:1.

(by default) due to chloride depletion. That is, a 1:1 Cl⁻:Br⁻ stoichiometric reaction has occurred during oxidation in the mixed salt experiments. This result is important since it reveals that an equal molar mixture of chloride and bromide is present in the oxidation product(s) formed.

Additional information as to the identity of the mixed salt oxidation product(s) can be gained by noting that only trace amounts of BrO₃⁻, ClO₂⁻, and ClO₃⁻ ions were detected (less than 0.2 mole % relative to the total bromide present). The lack of BrO₃⁻ formation observed here is inconsistent with the study of Haag and Hoigne [1983] performed previously. A likely cause of this discrepancy is that the presence of chloride enables BrCl production to occur via reaction (6) above. The lack of ionic halogen-oxide product formation in our experiment is consistent with analyses of the effluent gas (which was scrubbed in a 0.1 M NaOH solution) that revealed a significant Br⁻ concentration (~30% of the total bromide present). Since the quantity of bromide oxidized was typically 40% of the amount initially present (for a 125 min. reaction time), 10% of the oxidized bromide remained in solution. The importance of this result cannot be overstated as it implies that a molecular neutral, and volatile, product was formed.

An estimate of the Henry's law solubility of BrCl can be obtained from the mass balance for BrCl:

$$\text{BrCl (in solution, 10\%)} = \text{BrCl (produced, 40\%)} - \text{BrCl (trapped, 30\%),} \quad (7)$$

where the percentages of each BrCl contribution were taken from the discussion above. The Henry's law solubility can be computed from the data in Figure 5, the ratio BrCl(in solution)/BrCl(trapped) by converting the volatile portion of BrCl into a partial pressure, and accounting for formation of the trihalide, $\text{BrCl} + \text{Cl}^- \leftrightarrow \text{BrCl}_2^-$ having $K_{\text{eq}} = 3.8 \text{ M}^{-1}$ [Liu and Margerum, 1998]. The resulting analysis yields a value of 1.5 M/atm for the Henry's law solubility of BrCl at 290 K.

In summary, experimental results presented here illustrate a non-linear dependence of the oxidation rate on bromide ion concentration. Our findings suggest that non-ideal solution behavior in aqueous sea-salt aerosol solutions may not enable a unique elementary reaction rate constant to be used in modeling simulations. Further studies of elementary reaction processes representative of solution concentrations to be encountered in the marine boundary layer are needed. In addition, a 1:1 Cl⁻:Br⁻ stoichiometric reaction to form a volatile halogen product is consistent with reactions (4)-(6), namely $2\text{H}^+ + \text{Br}^- + \text{Cl}^- + \text{O}_3 \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{BrCl}$. The identification of this reaction stoichiometry supports the chloride depletion mechanism (i.e., reaction (6)) proposed by Vogt et al. [1996] previously.

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W. R. Barchet, E. G. Chapman, S. D. Colson, and R. S. Disselkamp, Pacific Northwest National Laboratory, Richland, WA 99352. (e-mail: rich.barchet@pnl.gov; elaine.chapman@pnl.gov; steven.colson@pnl.gov; robert.disselkamp@pnl.gov)
 C. D. Howd, Department of Chemistry, University of Michigan at Flint, Flint, MI 48502. (e-mail: chowd@student.flint.umich.edu)

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