

# UC Irvine

## UC Irvine Previously Published Works

### Title

Bromine activation in the troposphere by the dark reaction of O<sub>3</sub> with seawater ice

### Permalink

<https://escholarship.org/uc/item/94t150pr>

### Journal

Geophysical Research Letters, 25(21)

### ISSN

00948276

### Authors

Oum, K. W  
Lakin, M. J  
Finlayson-Pitts, B. J

### Publication Date

1998-11-01

### DOI

10.1029/1998GL900078

Peer reviewed

## Bromine activation in the troposphere by the dark reaction of O<sub>3</sub> with seawater ice

K. W. Oum, M. J. Lakin and B. J. Finlayson-Pitts

Department of Chemistry, University of California, Irvine, CA 92697-2025

**Abstract.** There is increasing evidence that bromine atoms play a role in tropospheric chemistry in the marine boundary layer. In addition, they are believed to lead to rapid depletion of surface level ozone in the Arctic at polar sunrise. While mechanisms have been proposed for recycling bromine atoms from sea salt particles, the initial reaction(s) leading to the formation of bromine atom precursors is not known. We report here the formation of gaseous Br<sub>2</sub> from the reaction of seawater ice with O<sub>3</sub> in the dark. These observations suggest that this reaction is a potential source of tropospheric photolyzable bromine in high latitude coastal regions in winter. In addition, it may be the source of the photolyzable bromine gas measured recently in the Arctic by Impey et al. (1997), which is believed to be responsible for the ozone destruction at polar sunrise.

### Introduction

Episodes of rapid depletion of surface level ozone in the Arctic at polar sunrise were reported a number of years ago (Bottenheim and Gallant, 1986; Oltmans and Komhyr, 1986). Barrie and coworkers (1988) attributed this rapid ozone loss to gas phase bromine chemistry. This has been confirmed by the recent measurement both before and during ozone destruction of unspecified photolyzable bromine atom precursors, suggested to be Br<sub>2</sub> and/or HOBr (Impey et al., 1997). BrO, an intermediate in the chain reactions, has also been observed during periods of ozone destruction (e.g. see Platt and Hausmann, 1994; Hausmann and Platt, 1994; Tuckermann et al., 1997; Richter et al., 1998).

While gas phase bromine reactions terminate in the form of products such as HBr, BrONO<sub>2</sub> and HOBr, there are mechanisms for recycling bromine during periods of ozone destruction. For example, McConnell et al. (1992) suggested that HBr as well as organic bromine compounds would be taken up by aerosol particles and ice crystals. This condensed phase bromine was thought to be subsequently converted to Br<sub>2</sub>, which Fan and Jacob (1992) proposed could occur by the reaction of HBr in particles with HOBr. Such a mechanism is consistent with the known aqueous phase reaction of HOBr with Br<sup>-</sup> (Eigen and Kustin, 1962), as well as with the rapid reaction of HOBr with ice containing HCl, HBr, NaCl or NaBr to generate Br<sub>2</sub> (Abbatt, 1994; Kirchner et al., 1997). LeBras and Platt (1995) proposed a gas phase BrO + ClO radical chain to recycle bromine, similar to that which takes place in the stratosphere (Yung et al., 1980).

Recently, Crutzen and coworkers (Sander and Crutzen, 1996; Vogt et al., 1996) developed a comprehensive chemical box model for halogen chemistry in the marine boundary layer in

which gaseous HOBr is taken up into aerosol particles, converted to BrCl and Br<sub>2</sub>, and released to the gas phase. Such processes are clearly relevant to halogen chemistry in the Arctic boundary layer at polar sunrise as well.

The original source of bromine atoms needed to initiate the chain destruction of ozone remains controversial (Niki and Becker, 1994). The photolysis of bromoform, as originally proposed (Barrie et al., 1988), appears to be too slow. However, Tang and McConnell (1996) have proposed that it might still be sufficient if it activates chain reactions involving bromide from sea salt particles accumulated on the snow pack during polar winter. Chlorine atom chemistry has also been observed simultaneously with the ozone depletion episodes (Jobson et al., 1994), supporting sea salt as the bromine source. Consistent with this, Hopper et al. (1998) observed that the ozone depleting processes occurred only in air masses above sea ice. Mozurkewich (1995) proposed oxidation of sea salt bromide by peroxymonosulfuric acid, which would presumably require the presence of significant amounts of SO<sub>2</sub>.

We report here the results of laboratory studies which indicate that gaseous Br<sub>2</sub> is generated by a dark reaction of O<sub>3</sub> with bromide in sea salt ice. As discussed in more detail below, this potential source of bromine atoms is consistent with the recent suggestion by Impey et al. (1997) who, based on work by Taube (1942), proposed the formation of Br<sub>2</sub> from the ozone oxidation of Br<sup>-</sup> originating from seawater.

### Experimental

Solutions of synthetic (Instant Ocean®) or authentic sea salt were prepared by dissolving the salt (50-300 g) in 1.8 L of Nanopure water (Barnstead, ρ > 18 MΩ) (pH 8). The authentic sea salt was obtained by filtering sea water collected off the coast of southern California and evaporating the water. Solutions were frozen at 193 K in a 37 x 27 x 5 cm container. The frozen solutions were removed from the freezer and placed on a metal support which had cooling channels through which a cooled fluid was circulated at 273 K to minimize melting of the ice during the experiment. The cooling panel and frozen solution were placed inside a 45 L Teflon reaction chamber, and a mixture of O<sub>3</sub> and UHP air was flowed over the frozen ice surface at a typical flow rate of 3 L min<sup>-1</sup>. Although the higher temperature of the gases relative to the ice surface resulted in warming above the original freezing temperature of 193 K, the surface of the ice always remained frozen below 272 K in these experiments.

A low pressure mercury lamp (UV Products, Inc., Model PCQX1) was mounted above the ice to irradiate the ice-O<sub>3</sub> mixture at 254 nm. Radiation at 254 nm was used as it generates OH from O<sub>3</sub> photolysis but does not photolyze Br<sub>2</sub>, Cl<sub>2</sub> or BrCl. The concentrations of O<sub>3</sub> were measured at the exit using an ozone monitor (Dasibi, Model 1003-AH). The mixtures of unreacted O<sub>3</sub> and product gases exiting the chamber were monitored using

Copyright 1998 by the American Geophysical Union.

Paper number GRL-1998900078.  
0094-8276/98/GRL-1998900078\$05.00

atmospheric pressure ionization mass spectrometry (API-MS). This is a tandem mass spectrometer in which ions selected using the first quadrupole can be collisionally dissociated and the fragments measured using the second quadrupole (the MS-MS mode). Use of the first quadrupole alone gives a conventional mass spectrum. Chemical ionization for the gases of interest here, Br<sub>2</sub>, BrCl and Cl<sub>2</sub>, occurs in the negative ion mode by electron transfer from O<sub>2</sub><sup>-</sup> and its clusters, formed by a corona discharge in the air mixture (Spicer et al., 1998).

## Results and Discussion

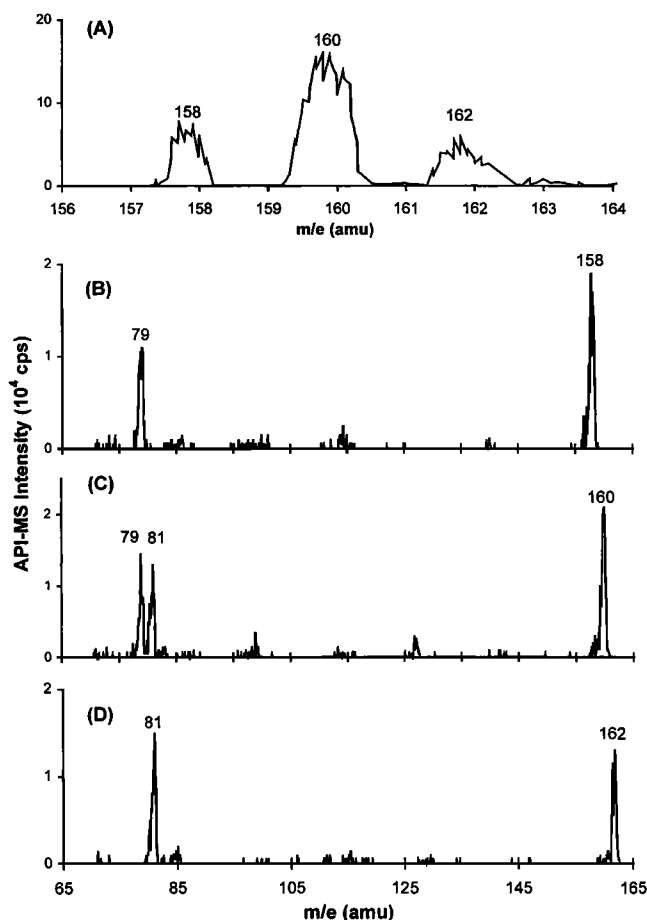
Figure 1 shows the conventional mass spectrum (A) as well as MS-MS spectra (B-D) when O<sub>3</sub> at 1.8 ppm passed over frozen synthetic sea salt in the dark. Peaks due to Br<sub>2</sub> were formed in the dark in the presence of O<sub>3</sub>. Similar results were obtained using ice prepared with authentic sea salt collected off the coast of southern California. Br<sub>2</sub> production did not change significantly over the range of salt concentrations from 28-170 g L<sup>-1</sup>.

Figure 2 shows the ion count at *m/e* = 160 due to Br<sub>2</sub> as variable O<sub>3</sub> concentrations flowed over frozen synthetic sea salt in the dark. There were no detectable peaks from Cl<sub>2</sub> (detection limit ~50 ppt) with or without irradiation.

The formation of Br<sub>2</sub> in the dark is consistent with the known aqueous phase reactions, summarized in Table 1. O<sub>3</sub> is well known to oxidize Br<sup>-</sup> in solution to OBr<sup>-</sup> (Taube, 1942; Haag and Hoigné, 1983; von Gunten and Hoigné, 1994). The pK<sub>a</sub> for HOBr is 8.8, so that at a pH of 8, typical of seawater, the ratio [HOBr]/[OBr<sup>-</sup>] = 6.3. Thus, once bromide is oxidized by ozone, HOBr is formed. The HOBr can react with either Cl<sup>-</sup> or Br<sup>-</sup>. Recent studies of the reactions of HOBr with bromide and chloride in ice, either as HBr/HCl (Abbatt, 1994) or as NaBr/NaCl (Kirchner et al., 1997) show that the reaction probabilities for HOBr with Br<sup>-</sup> and Cl<sup>-</sup> are within a factor of approximately three of each other. In seawater, the molar ratio of Cl<sup>-</sup> to Br<sup>-</sup> is 658:1. Given the similar reaction probabilities, the major fate of HOBr is expected to be reaction with Cl<sup>-</sup> to generate BrCl. (However, as discussed below, the ice surface is expected to be enriched in bromide relative to chloride, which may increase the relative importance of the bromide reaction. Unfortunately, measurements of the surface composition are not available to quantify this.)

The equilibria and reaction kinetics of BrCl in aqueous solutions at 298 K and an ionic strength of 1.0 M have been reported by Margerum and coworkers (Wang et al., 1994). In aqueous solution, BrCl rapidly hydrolyzes ( $k > 10^5$  s<sup>-1</sup>) to form HOBr. Alternatively, it reacts rapidly with Br<sup>-</sup>, generating Br<sub>2</sub>Cl<sup>-</sup> which dissociates to Br<sub>2</sub> and Cl<sup>-</sup>. The alternate reaction (8) of BrCl with Cl<sup>-</sup> to give BrCl<sub>2</sub><sup>-</sup> also leads to HOBr, since BrCl<sub>2</sub><sup>-</sup> hydrolyzes to HOBr (reaction 9). In short, assuming that the equilibrium constants for reactions (2)-(9) do not change significantly relative to each other as the temperature is lowered, the equilibria in the aqueous phase favor production of Br<sub>2</sub> in the dark, despite the large molar ratio of chloride to bromide in seawater. Doping with additional NaBr increased the production of Br<sub>2</sub>, consistent with enhancement of reaction (3) of HOBr with Br<sup>-</sup> to form Br<sub>2</sub>.

Upon irradiation at 254 nm, used to photolyze O<sub>3</sub> but not the product species Br<sub>2</sub>, BrCl, or possibly Cl<sub>2</sub>, small amounts of BrCl and peaks tentatively assigned to HOBr (T. Caldwell, J. C. Hemminger and B. J. Finlayson-Pitts, unpublished data, 1998) were further formed. At 254 nm, gaseous O<sub>3</sub> generates O(<sup>1</sup>D) which reacts with water vapor to form OH. Although Br<sub>2</sub> does not photolyze at 254 nm, the reaction of OH with Br<sub>2</sub> in the gas phase to form HOBr + Br is fast ( $k^{298} = 4.2 \times 10^{-11}$  cm<sup>3</sup> mole-

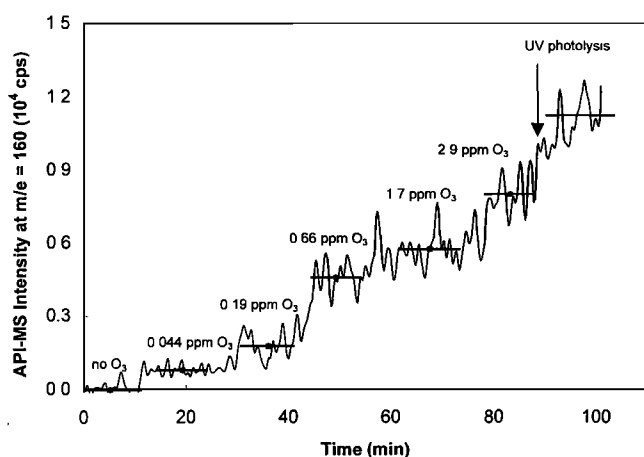


**Figure 1.** Atmospheric pressure ionization mass spectrometer (API-MS) spectra of Br<sub>2</sub> formed in the reaction of 1.8 ppm O<sub>3</sub> with sea salt ice [170 g L<sup>-1</sup> synthetic sea salt (Instant Ocean®)] at a relative humidity (RH) of 20%. (A) Conventional MS of the Br<sub>2</sub> region (30 scans coadded); (B)-(D) MS-MS scans of peaks *m/e* = 158, 160 and 162 respectively (100 scans coadded). The observation of fragments at 79 and 81 confirm the production of Br<sub>2</sub>.

cule<sup>-1</sup> s<sup>-1</sup>) (Atkinson et al., 1997). This is a likely additional source of gas phase HOBr under irradiation.

Our previous studies showed that Cl<sub>2</sub> is produced at room temperature upon irradiation of mixtures of ozone and aqueous seasalt particles suspended in air (Oum et al., 1998). The oxidation of Cl<sup>-</sup> by O<sub>3</sub> itself is known to be slow (Hoigné et al., 1985), so that Cl<sub>2</sub> is likely formed by secondary reactions, for example, involving OH. Cl<sub>2</sub> was not detected here upon irradiation, which may reflect slower reactions in ice and at the lower temperature of these experiments. In addition, if small amounts of Cl<sub>2</sub> were generated in the ice surface layer, the fast reaction with Br<sup>-</sup> in the bulk (Wang et al., 1994) and at the interface (Hu et al., 1995) would form BrCl<sub>2</sub><sup>-</sup> which is in equilibrium with BrCl and Cl<sup>-</sup>. Reaction at the interface in particular could lead to the very small amounts of gaseous BrCl observed upon irradiation.

This trapping and reaction of photochemically generated Cl<sub>2</sub> will be enhanced if the surface layer is enriched in bromide ion. As the seawater solution freezes, water will first solidify, excluding salts to the surrounding aqueous phase. The solubility of NaBr in water near 0°C is larger than that of NaCl (45 versus 26 weight %) (Stephen and Stephen, 1963), and the eutectic point of NaBr in aqueous solution is 7 K lower than that of NaCl (Laidler and Meiser, 1982). As the temperature falls further, NaCl will begin to crystallize out. Finally, bromide will begin to crystallize



**Figure 2.** The production of Br<sub>2</sub> from seawater ice (40 g L<sup>-1</sup>) at increasing O<sub>3</sub> concentrations. The start time for UV photolysis is indicated with an arrow. Horizontal lines are drawn to indicate times of relatively constant ozone concentrations.

at even lower temperatures. This leaves an aqueous phase enriched not only in overall salt concentration but also in bromide relative to chloride which would be retained as the ice surface warmed during the experiments. Starting with the same relative concentration of bromide and chloride, the halide surface concentration is expected to be relatively constant for different salt concentrations, consistent with the observed insensitivity of Br<sub>2</sub> produced to the initial seawater concentration. It is noteworthy that enrichment of bromide in the surface layer of the Arctic snowpack, possibly resulting from the ice freezing process or by atmospheric deposition of aerosols enriched in bromide, has been observed (Ariya et al., 1998).

The temperature at the frozen seawater surface in our experiments was typically between 268–272 K, where the ice surface is

often described as a quasi-liquid layer (Hobbs, 1973). The thickness of the quasi-liquid layer depends on both temperature and the concentration of solutes. Even at a bulk NaCl concentration of 10<sup>-3</sup> M, the thickness of the quasi-liquid layer is increased by a factor of six over pure water at 270 K and a factor of three at 243 K (Conklin and Bales, 1993). Our experiments did not examine Br<sub>2</sub> production at 245 K, typical of the Arctic at polar sunrise. However, it is not unreasonable that it also occurs at these temperatures since bromine chemistry similar to that in the aqueous phase, and proposed here, has been observed on ice surfaces at 228 and 240 K (Abbatt, 1994; Kirchner et al., 1997), possibly in a quasi-liquid layer which is expected to exist even at these lower temperatures (Conklin and Bales, 1993).

Our results suggest that the dark reaction of O<sub>3</sub> with seawater ice will generate Br<sub>2</sub> in high latitude coastal regions in winter. In addition, the conditions of our experiments may be similar to that of seawater ice adjacent to regions of open water (polynyas) found in the Arctic between Greenland and Ellesmere Island, the region where surface-level ozone depletion has been observed to occur (Hopper et al., 1998). It may be relevant that Richter et al. (1998) report, based on satellite data, that enhanced tropospheric BrO in the Arctic spring follows not only increasing light intensity but also the region of retreating sea ice. The reaction could involve not only the surface of frozen seawater, but also sea salt deposited on the ice or snow pack and/or saline frost flowers formed by ice growth near leads (Perovich and Richter-Menge, 1994).

The production of Br<sub>2</sub> from the reaction of O<sub>3</sub> with frozen seawater is consistent with the observations of Impey et al. (1997) who report the formation of an unidentified photolyzable bromine compound. Particularly relevant is the observation by Impey and coworkers that the concentration of the bromine species declined as O<sub>3</sub> was destroyed, and increased as O<sub>3</sub> increased, suggesting that ozone is at least partly involved in the formation of the bromine compound(s).

**Table 1.** Aqueous Phase Chemistry of O<sub>3</sub> and Bromide

Reaction Number	Reaction	Equilibrium (K) or Rate (k) Constant <sup>a</sup>	Reference
1	O <sub>3</sub> + Br <sup>-</sup> → OBr <sup>-</sup> + O <sub>2</sub>	k <sub>1</sub> = 53 M <sup>-1</sup> s <sup>-1</sup> <sup>b</sup>	Haag & Hoigné, 1983
2	OBr <sup>-</sup> + H <sup>+</sup> ↔ HOBr	K <sub>2</sub> = 10 <sup>8</sup> <sup>8</sup>	Haag & Hoigné, 1983
3	HOBr + Br <sup>-</sup> → Br <sub>2</sub> + OH <sup>-</sup>	γ <sub>ice</sub> = (3.3 × 10 <sup>-3</sup> ) - 0.12 <sup>c</sup> k = 1.6 × 10 <sup>2</sup> M <sup>-1</sup> s <sup>-1</sup> <sup>d</sup>	Abbatt, 1994; Kirchner et al., 1997 Eigen and Kustin, 1962
4	HOBr + Cl <sup>-</sup> → BrCl + OH <sup>-</sup>	γ <sub>ice</sub> = (1.2 × 10 <sup>-3</sup> ) - 0.25 <sup>c</sup>	Abbatt, 1994; Kirchner et al., 1997
5	BrCl + H <sub>2</sub> O ↔ HOBr + Cl <sup>-</sup> + H <sup>+</sup>	K <sub>5</sub> = 1.8 × 10 <sup>-5</sup> M <sup>2</sup> k <sub>5</sub> > 10 <sup>5</sup> s <sup>-1</sup>	Wang et al., 1994
6	BrCl + Br <sup>-</sup> ↔ Br <sub>2</sub> Cl <sup>-</sup>	K <sub>6</sub> = 1.8 × 10 <sup>4</sup> M <sup>-1</sup> k <sub>6</sub> > 10 <sup>8</sup> M <sup>-1</sup> s <sup>-1</sup>	Wang et al., 1994
7	Br <sub>2</sub> Cl <sup>-</sup> ↔ Br <sub>2</sub> + Cl <sup>-</sup>	K <sub>7</sub> = 1.3 M	Wang et al., 1994
8	BrCl + Cl <sup>-</sup> ↔ BrCl <sub>2</sub> <sup>-</sup>	K <sub>8</sub> = 6.0 M <sup>-1</sup>	Wang et al., 1994
9	BrCl <sub>2</sub> <sup>-</sup> + H <sub>2</sub> O ↔ HOBr + H <sup>+</sup> + 2 Cl <sup>-</sup>	K <sub>9</sub> = 3.0 × 10 <sup>-6</sup> M <sup>3</sup>	Wang et al., 1994

<sup>a</sup>At room temperature unless otherwise noted.

<sup>b</sup>Calculated at 0°C using E<sub>a</sub> = 37 kJ mole<sup>-1</sup> and A = 6.3 × 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup> (Haag & Hoigné, 1983).

<sup>c</sup>Reactions with HBr and HCl carried out at 228 K (Abbatt, 1994) and with NaBr and NaCl in ice at 240 K (Kirchner et al., 1997); higher reaction probabilities occur for the HCl and HBr due to acid catalysis.

<sup>d</sup>Calculated using k(HOBr + Br<sup>-</sup> + H<sup>+</sup>) = 1.6 × 10<sup>10</sup> M<sup>-2</sup> s<sup>-1</sup> and a pH = 8.

In our sea salt ice laboratory experiments, an average steady-state concentration of  $(16 \pm 8)$  ppt ( $\pm 2\sigma$ ) Br<sub>2</sub> was generated from the dark reaction of 40 ppb O<sub>3</sub> with an ice surface of area 10<sup>3</sup> cm<sup>2</sup>. The dilution rate constant was estimated to be  $1.1 \times 10^{-3} \text{ s}^{-1}$ , so that the net rate of production was  $4.4 \times 10^5$  molecules cm<sup>-3</sup> s<sup>-1</sup>, or taking into account the 45 L volume, a total of  $2 \times 10^{10}$  molecules s<sup>-1</sup> or  $2 \times 10^7$  molecules s<sup>-1</sup> per cm<sup>2</sup> of ice surface. Assuming that Br<sub>2</sub> is emitted into an air mass with 400 m mixing height (Hopper et al., 1998) the amount of Br<sub>2</sub> which would be formed in 10 hours is 0.6 ppt, approximately equal to the concentration shown in the Tang and McConnell model to be sufficient to initiate ozone depletion.

In summary, the dark reaction of O<sub>3</sub> with frozen seawater forms Br<sub>2</sub> which, upon photolysis, generates atomic bromine. This reaction likely occurs in high latitude coastal regions in winter. It is also consistent with recent field observations of the behaviour of the bromine source responsible for surface level ozone depletion in the Arctic at polar sunrise (Impey et al., 1997; Hopper et al., 1998; Richter et al., 1998).

**Acknowledgments.** The authors are grateful to the National Science Foundation, the Department of Energy and the University of California, Irvine for support of this work. We also thank L. E. Overman for providing a low temperature control, J. N. Pitts, Jr., T. Benter and D. O. DeHaan for helpful discussions, P. B. Shepson, G. W. Harris, P. Ariya and W. S. Reebergh for providing additional data and insights into Arctic chemistry, and A. Richter for providing a preprint prior to publication.

## References

- Abbatt, J., Heterogeneous reaction of HOBr with HBr and HCl on ice surfaces at 228 K, *Geophys. Res. Lett.* 21, 665-668, 1994.
- Ariya, P. A., J. F. Hopper and G. W. Harris, "Hydrocarbon concentration in Arctic snowpack interstitial air", presented at the EGS XXIII General Assembly, Nice, France, April 20-24, 1998.
- Atkinson, R., D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, M. J. Rossi and J. Troe, Evaluated kinetic, photochemical and heterogeneous data for atmospheric chemistry: supplement V, IUPAC subcommittee on gas kinetic data evaluation for atmospheric chemistry, *J. Phys. Chem. Ref. Data* 26, 521-1011, 1997.
- Barrie, L. A., J. W. Bottenheim, R. C. Schnell, P. J. Crutzen and R. A. Rasmussen, Ozone destruction and photochemical reactions at polar sunrise in the lower Arctic atmosphere, *Nature* 334, 138-141, 1988.
- Bottenheim, J. W. and A. G. Gallant, Measurements of NO<sub>y</sub> species and O<sub>3</sub> at 82° N latitude, *Geophys. Res. Lett.* 13, 113-116, 1986.
- Conklin, M. H. and R. C. Bales, SO<sub>2</sub> uptake on ice spheres: Liquid nature of the ice-air interface, *J. Geophys. Res.* 98, 16851-16855, 1993.
- Eigen, M. and K. Kustin, The kinetics of halogen hydrolysis, *J. Am. Chem. Soc.* 84, 1355-1361, 1962.
- Fan, S.-M. and D. J. Jacob, Surface ozone depletion in Arctic spring sustained by bromine reactions on aerosols, *Nature* 359, 522-524, 1992.
- Finlayson-Pitts, B. J., F. E. Livingston and H. N. Berko, Ozone destruction and bromine photochemistry at ground level in the Arctic spring, *Nature* 343, 622-625, 1990.
- Haag, W. R. and J. Hoigné, Ozonation of bromide-containing waters: Kinetics of formation of hypobromous acid and bromate, *Environ. Sci. Technol.* 17, 261-267, 1983.
- Hausmann M. and U. Platt, Spectroscopic measurement of bromine oxide and ozone in the high Arctic during Polar Sunrise Experiment 1992, *J. Geophys. Res.* 99, 25399-25413, 1994.
- Hobbs, P. V. *Ice Physics*, 837 pp., Clarendon Press, Oxford, U. K. 1973.
- Hoigné, J., H. Bader and W. R. Haag, Rate constants of reactions of ozone with organic and inorganic compounds in water - III: Inorganic compounds and radicals, *Water Res.* 19, 993-1004, 1985.
- Hopper, J. F., L. A. Barrie, A. Siliis, W. Hart, A. J. Gallant and H. Dryfhout, Ozone and meteorology during the 1994 Polar Sunrise Experiment, *J. Geophys. Res.* 103, 1481-1492, 1998.
- Hu, J. H., Q. Shi, P. Davidovits, D. R. Worsnop, M. S. Zahniser and C. E. Kolb, Reactive uptake of Cl<sub>2</sub> (g) and Br<sub>2</sub> (g) by aqueous surfaces as a function of Br<sup>-</sup> and I<sup>-</sup> ion concentration: The effect of chemical reaction at the interface, *J. Phys. Chem.* 99, 8768-8776, 1995.
- Impey, G. A., P. B. Shepson, D. R. Hastie, L. A. Barrie, and K. Anlauf, Measurements of photolyzable chlorine and bromine during the polar sunrise experiment, 1995, *J. Geophys. Res.* 102, 16005-16010, 1997.
- Jobson, B. T., H. Niki, Y. Yokouchi, J. Bottenheim, F. Hopper and R. Leitch, Measurements of C2-C6 hydrocarbons during the polar sunrise 1992 experiment: Evidence for Cl atom and Br atom chemistry, *J. Geophys. Res.* 99, 25355-25368, 1994.
- Kirchner, U., Th. Benter and R. N. Schindler, Experimental verification of gas phase bromine enrichment in reactions of HOBr with sea salt doped ice surfaces, *Ber. Bunsenges. Phys. Chem.* 101, 975-977, 1997.
- Laidler, K. J. and J. H. Meiser, *Physical Chemistry*, 919 pp., Benjamin/Cummings, Menlo Park, CA, 1982.
- LeBras, G. and U. Platt, A possible mechanism for combined chlorine and bromine catalyzed destruction of tropospheric ozone in the Arctic, *Geophys. Res. Lett.* 22, 599-602, 1995.
- McConnell, J. C., G. S. Henderson, L. Barrie, J. Bottenheim, H. Niki, C. H. Langford and E. M. J. Templeton, Photochemical bromine production implicated in Arctic boundary-layer ozone depletion, *Nature* 355, 150-152, 1992.
- Mozurkewich, M., Mechanisms for the release of halogens from sea-salt particles by free radical reactions, *J. Geophys. Res.* 100, 14199-14207, 1995.
- Niki, H. and K. H. Becker (Eds.), *The Tropospheric Chemistry of Ozone in the Polar Regions*, NATO ASI Series, Series I, Vol. 7, 425 pp., Springer-Verlag, Berlin, 1993.
- Oltmans, S. J. and W. D. Komhyr, Surface ozone distributions and variations from 1973-1984 measurements at the NOAA Geophysical Monitoring for Climatic Change Baseline Observatories, *J. Geophys. Res.* 91, 5229-5236, 1986.
- Oum, K. W., M. J. Lakin, D. O. DeHaan, T. Brauers and B. J. Finlayson-Pitts, Formation of molecular chlorine from the photolysis of ozone and aqueous sea-salt particles, *Science* 279, 74-77, 1998.
- Perovich, D. K. and J. A. Richter-Menge, Surface characteristics of lead ice, *J. Geophys. Res.* 99, 16341-16350, 1994.
- Platt U. and M. Hausmann, Spectroscopic measurement of the free radicals NO<sub>3</sub>, BrO, IO, and OH in the troposphere, *Res. Chem. Intermed.* 20, 557-578, 1994.
- Richter, A., F., F. Wittrock, M. Eisinger and J. P. Burrows, GOME observations of tropospheric BrO in northern hemispheric spring and summer 1997, *Geophys. Res. Lett.* 25, 2683-2686, 1998.
- Sander, R. and P. J. Crutzen, Model study indicating halogen activation and ozone destruction in polluted air masses transported to the sea, *J. Geophys. Res.* 101, 9121-9138, 1996.
- Spicer C. W., E. G. Chapman, B. J. Finlayson-Pitts, R. A. Plastringe, J. M. Hubbe, J. D. Fast and C. M. Berkowitz, Unexpectedly high concentrations of molecular chlorine in coastal air, *Nature* 394, 353-356, 1998.
- Stephen, H. and T. Stephen (Eds.), *Solubilities of Inorganic and Organic Compounds*, Pergamon Press, Oxford, 1963.
- Tang, T. and J. C. McConnell, Autocatalytic release of bromine from Arctic snow pack during polar sunrise, *Geophys. Res. Lett.* 23, 2633-2636, 1996.
- Taube, H. Reactions in solutions containing O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, H<sup>+</sup>, and Br<sup>-</sup>. The specific rate of the reaction O<sub>3</sub> + Br<sup>-</sup>, *J. Am. Chem. Soc.* 64, 2468-2474, 1942.
- Tuckermann, M., R. Ackermann, C. Götz, H. Lorenzen-Schmidt, T. Senne, J. Stutz, B. Trost, W. Unold, and U. Platt, DOAS-observation of halogen radical-catalyzed Arctic boundary layer ozone destruction during the ARCTOC campaigns 1995 and 1996 in Ny-Ålesund, Spitsbergen, *Tellus* 49B, 533-555, 1997.
- Vogt, R., P. J. Crutzen and R. Sander, A mechanism for halogen release from sea-salt aerosol in the remote marine boundary layer, *Nature* 383, 327-330, 1996.
- von Gunten, U. and J. Hoigné, Bromate formation during ozonation of bromide-containing waters: Interaction of ozone and hydroxyl radical reactions, *Environ. Sci. Technol.* 28, 1234-1242, 1994.
- Wang, T. X., M. D. Kelley, J. N. Cooper, R. C. Beckwith and D. W. Margerum, Equilibrium, kinetic and UV-spectral characteristics of aqueous bromine chloride, bromine and chlorine species, *Inorg. Chem.* 33, 5872-5878, 1994.
- Yung, Y. L., J. P. Pinto, R. T. Watson and S. P. Sander, Atmospheric bromine and ozone perturbations in the lower stratosphere, *J. Atmos. Sci.* 37, 339-353, 1980.

B. J. Finlayson-Pitts, M. J. Lakin, and K. W. Oum, Department of Chemistry, University of California, Irvine, CA 92697-2025.  
(email: bjfinlay@uci.edu, mlakin@uci.edu, koum@uci.edu)

(Received June 26, 1998; accepted August 24, 1998.)