Mechanisms for the release of halogens from sea-salt particles by free radical reactions

Michael Mozurkewich
Department of Chemistry and Centre for Atmospheric Chemistry, York University, North York, Ontario, Canada

Abstract A possible source of gas phase bromine in the Arctic winter and early spring is the sea-salt aerosol. In this paper, chemical mechanisms for the release of photochemically active bromine from sea-salt are examined. The first of these is oxidation of bromide to elemental bromine by peroxymonosulfuric acid (Caro's acid) produced by the free radical chain oxidation of S(IV). The chain reaction could be initiated in the dark by NO2 or, following polar sunrise, by the reaction of ozone with superoxide. Although the yield of Caro's acid at 298 K is small, the yield may increase at the low temperatures encountered in the Arctic. This could result in the conversion of a large fraction of the initial sea-salt alkalinity to Caro's acid. Caro's acid is known to oxidize bromide to Br2. Since this mechanism requires low temperatures and high SO2 concentrations, it is only effective during the winter and early spring and should not oxidize significant amounts of halides in the global marine boundary layer. A second possible mechanism is the free radical oxidation of aqueous bromide to bromine by OH and HO:. This may be effective at moderate pH and may contribute to Br cycling on a global scale. The evaluation of both mechanisms is highly uncertain because of incomplete physical-chemical data. In addition to these primary release mechanisms, there are possible autocatalytic cycles for the release of bromine from sea-salt. These involve the gas phase production of either BrO or HOBr and the return of these species to the sea-salt particles where they initiate additional oxidation of bromide. The efficiency of these cycles should depend critically on the relative amounts of HOBr and HBr produced by the gas phase chemistry. These mechanisms do not appear to be effective as sources of photochemically active Cl.

Introduction

A dramatic loss of surface layer ozone has been observed shortly after polar sunrise in the Arctic [Bottenheim et al., 1990]. This loss is associated with a large increase in the amount of "filterable" Br present in the atmosphere. Barrie et al. [1988] have proposed that the ozone loss is caused by a catalytic cycle involving Br atoms. There is also evidence for halogen atom oxidation of hydrocarbons during polar sunrise [Jobson et al., 1994]. It appears that the filterable Br is inorganic but is not HBr; this implies that it is in a photochemically active form, such as HOBr or Br2 [Li et al., 1994].

Computational studies [Barrie et al., 1988; McConnell et al., 1992; Fan and Jacob, 1992] have shown that the observed filterable Br can produce significant ozone loss if it is in a photochemically active form. Reactions with hydrocarbons eventually convert the active Br into inactive HBr; the HBr returns to the particle phase. As a result, these models require a means of recycling HBr into an active form; a variety of proposals have been made as to how this is accomplished. The models assume an initially high concentration of active gas phase Br.

The initial source of the filterable Br has not yet been identified. The air masses do contain particulate Na; this is presumably from sea-salt. However, the Br/Na ratios reported by Bottenheim et al. [1990] are typically about a factor of 5 larger than in sea-salt. The Na size distributions imply that the sea-salt aerosol is well aged and that much of the original sea-salt has been lost. This is reasonable since this aerosol must have been transported a substantial distance from the ocean areas. If sea-salt is the original source of the Br2, then the lifetime of Br in the air mass must be much longer than that of sea-salt. This implies that the Br is efficiently recycled, perhaps by the mechanism of Fan and Jacob [1992]. Here I propose a mechanism by which the bromine is released from sea-salt particles shortly after their formation.

The basic features of this mechanism are the following: (1) Gas phase free radicals are efficiently trapped in sea-salt aerosol particles. (2) These radicals induce the free radical chain oxidation of dissolved SO2. (3) One product of this chain reaction is peroxymonosulfuric acid, H2SO5, also known as Caro's acid; this can oxidize bromide ions to hypobromous acid, HOBr. (4) Subsequent reaction of HOBr with bromide ions results in the release of readily photolyzed bromine molecules to the gas phase. (5) In addition, at lower pH where the free radical chain reaction is not effective, radical-radical reactions can directly produce Br2. (6) Finally, the return of BrO or HOBr to sea-salt particles can release additional Br2 in a potentially autocatalytic cycle. Steps (5) and (6) may also help to reactivate Br after it is converted to HBr by gas phase...
photochemistry. Most of the individual processes have been previously recognized as being important in cloud water chemistry [Jacob, 1986; McElroy, 1986; Chameides and Stelson, 1992] or as a means of recycling Br in the Arctic [Fan and Jacob, 1992]. However, the potential for these processes to provide an initial source of active Br has not been recognized.

Release of Halogens from Sea-Salt Particles as a Result of Sulfur Oxidation

I assume here that the initial release of Br is from liquid sea-salt aerosol particles. It is reasonable to assume that these particles are liquid rather than crystalline even though the typical temperatures of the Arctic spring (230 to 250 K) are below the eutectic point for NaCl solutions (252 K). Small droplets have a pronounced tendency to both supercool and become supersaturated. Also, although the absolute humidity of Arctic air is low, the relative humidity, which determines if salt particles will deliquesce, is high. Since the particles are formed as liquid drops, they may well remain liquid throughout their residence time in the atmosphere.

The chemical reactions occurring in sea-salt particles are very different from those occurring in sulfate aerosol particles. For the purpose of the estimates to be made here, I assume that the sea-salt particles have the same composition as the "low relative humidity" case (80% RH) of Chameides and Stelson [1992]. This gives an ionic strength of 4.6 M, [Na+] = 3.6 M, [Br] = 4.7x10^-3 M, and an initial alkalinity of 0.013 M. For the present rough calculations, all activity coefficients are set equal to unity. This should not produce excessive errors for neutral and singly charged species. The only doubly charged ion that affects the chemistry considered here is SO4^2-; the effect of ionic strength on S(IV) equilibria can be accounted for by using the equilibrium constants measured by Millero et al. [1989] in concentrated NaCl solutions. Although the use of activities would result in more accurate concentrations, the results of rate calculations would not necessarily be improved.

The gas solubilities used here are given in Table 1, equilibrium constants for rapid liquid phase equilibria are given in Table 2, and liquid phase rate constants are in Table 3. Methods used to estimate temperature dependencies are discussed in Appendix A.

The initial pH of the droplets should be near that of seawater (pH=8) because of the presence of dissolved HCO3-. The alkalinity, A, of the initial drop is given by

\[ A = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \tag{1} \]

As CO2 is displaced from the drop by stronger acids, the pH slowly drops. Under polar sunrise conditions (200 ppt of SO2, 240 K), CO2 is almost completely displaced from the drops by SO2. The pH is then controlled by the S(IV) acid-base equilibria (E18) and (E19). This maintains the pH near 7. As SO3^2- is oxidized, the speciation among sulfur compounds changes so that

\[ A = [\text{HSO}_3^-] + 2[\text{SO}_3^{2-}] + 2[\text{SO}_4^{2-}] + [\text{HSO}_4^-] \tag{2} \]

The pH changes very slowly until the initial alkalinity is exhausted. The pH then drops rapidly as additional acid is produced. Because of the strong dependence of the solubility of S(IV) (i.e., the sum of SO2, HSO3-, and SO3^2-) on pH this produces a substantial change in the liquid phase chemistry.

The amount of time for which the pH remains high is determined by the rate of oxidation of S(IV). Chameides and Stelson [1992] found that oxidation by ozone, reaction (R1), can exhaust the buffering in a few minutes for conditions typical of the marine boundary layer. Although the rate constant for reaction (R1) is greatly reduced at low temperatures, this is partially compensated for by the increased gas solubilities. As a result, the buffering should be exhausted in a time that is much shorter than the particle lifetime. The uptake of gas phase acids, such as HNO3, should be negligible during this brief initial period.

S(IV) is also oxidized in a free radical chain reaction. This is initiated by reaction of SO3^2- with strongly oxidizing free radicals such as OH, Cl2', and Br2' (reactions (R17), (R18), and (R20)). The resulting sulfite radical rapidly adds O2 to form SO3-. The chain is propagated via

\[ \text{SO}_3^- + \text{SO}_3^- \rightarrow \text{SO}_4^{2-} + \text{SO}_3^- \tag{R13a} \]
\[ \text{SO}_3^- + \text{SO}_3^- \rightarrow \text{SO}_3^- + \text{SO}_4^{2-} \tag{R13b} \]
\[ \text{SO}_3^- + \text{SO}_3^- \rightarrow \text{SO}_3^- + \text{SO}_3^- \tag{R19} \]

Any radical-radical reaction could terminate the chain; reaction (R24) is the most probable because SO2 is the least reactive radical involved in the chain and is therefore present in the largest concentration. Caro's acid is produced by reaction (R13b) followed by equilibrium (E15).

Caro's acid is known to react with halide ions, e.g.,

\[ \text{HSO}_3^- + \text{Br}^- \rightarrow \text{SO}_4^{2-} + \text{HOBr} \tag{R3} \]

This leads to the production of elemental bromine via

\[ \text{HOBr} + \text{Br}^- + \text{H}^+ \rightarrow \text{Br}_2 + \text{H}_2\text{O} \tag{R6} \]

Br2 escapes to the gas phase where it is readily photolyzed to produce Br. At 298 K, with a typical seawater ratio of Cl to Br, roughly equal amounts of HOC1 and HOBr are produced by reactions (R2) and (R3). At 240 K, production of HOBr predominates. Under these conditions, substantial amounts of Cl2 are not produced until the Br is exhausted. The data of Jobson et al. [1994] implies a gas phase Br to Cl ratio between 400:1 and 1200:1.

There is a much larger flux of gas phase HO2 than OH to the drops. Although H2O and its conjugate base, O2-, are not particularly strong oxidants in solution, they can form more strongly oxidizing free radicals by means of the reactions

\[ \text{O}_2^- + \text{O}_3^- \rightarrow \text{O}_3^- + \text{O}_2^- \tag{R11} \]
\[ \text{O}_3^- + \text{H}^+ \rightarrow \text{OH}^- + \text{O}_2^- \tag{R12} \]

Lelieveld and Crutzen [1991] have argued that this is the dominant source of OH in cloud drops. As pointed out by Zafiriou [1974] and discussed further in the following
section, OH is rapidly and almost completely converted to \( \text{Br}_2 \) in seawater. Since \( \text{Br}_2 \) reacts rapidly with \( \text{SO}_3^+ \) (reaction (R20) and \( \text{SO}_3^2^- \)) is very large at pH 7 (nearly 1/2 the alkalinity), virtually every OH produced in solution should initiate the free radical chain reaction.

The upper limit to the number of free radical chains initiated by reaction (R11) is given by the flux of HO\(_2\) to the drop. Since sea-salt particle radii are much larger than mean free paths in air, the flux is determined primarily by gas phase diffusion [Schwartz, 1986]. Let \( \phi \) be the rate of transport of HO\(_2\) per unit liquid phase volume. Then if the partial pressure of HO\(_2\) is \( P_{\text{HO}_2} \) and the particle radius is \( a \), \( \phi \) is given by [Schwartz, 1986]

\[
\phi = \frac{3D_g P_{\text{HO}_2}}{a^2 RT} \tag{3}
\]

where \( D_g \) is the gas phase diffusion coefficient. For trace gases in air, \( D_g \) in units of cm\(^2\) s\(^{-1}\) may be estimated by

\[
D_g = (0.200) \left( \frac{T}{298} \right)^{1.75} \left( \frac{20}{M_w} \right)^{0.5} \tag{4}
\]

For 1 ppt of HO\(_2\) at 240 K with \( a = 2.0 \times 10^4 \) cm\(^2\), we have \( \phi = 1.0 \times 10^4 \) M s\(^{-1}\). For a steady state between this source and reaction (R11), if the drop is in equilibrium with 40 ppb of gas phase \( \text{O}_2 \), we have \( [\text{O}_2] = 4.5 \times 10^7 \) M.

In addition to undergoing reaction (R11), \( \text{HO}_2\text{(aq)} \) may either reevaporate from the drop or be consumed by reaction (R26). The characteristic time for reaction of \( \text{O}_2^* \) via (R11) is 0.45 s. Since this is much shorter than the gas phase mass transport characteristic time, \( (\text{H}_2\text{O}) \), of 180 s, the HO\(_2\) radicals do not reevaporate. This gas phase mass transport time is for diffusion of material from the drops, not from the gas phase to the drops. It therefore depends on gas solubility. The solubility is calculated using the effective Henry's law constant, \( H^* \); this includes the acid dissociation, equilibrium (E16). Since the time for reaction is much longer than the 0.7 ms characteristic time for liquid phase diffusion (Appendix B), the OH radicals are produced uniformly throughout the drop. At pH 7, [\( \text{HO}_2\)] is less than 1% of [\( \text{O}_2\)]. The resulting characteristic time for reaction of \( \text{O}_2^* \) via reaction (R26) is 6.5 s. Thus as long as the pH is high, over 90% of the HO\(_2\) radicals that enter the drop undergo reaction (R11) and the number of free radical chains initiated is near the upper limit.

The alkalinity of the drop determines how much S(IV) can be oxidized before the pH drops. The amount of Caro's acid produced is determined by the alkalinity and the competition between reaction (R13b) and reactions (R13a) and (R1). At 25 °C, \( k_{13c}/k_{13a} = 0.41 \) [Deister and Warneck, 1990]. Also, ozone oxidation tends to dominate over the free radical mechanism [Chameides and Stelson, 1992]. Thus the yield of Caro's acid is only about 4% of \( \text{H}_2\text{SO}_4 \). However, the yield may be substantially different at lower temperatures. The activation energies for reactions (R13b) and (R13a) estimated in Appendix A yield \( k_{13c}/k_{13a} = 11 \) at 240 K. Thus the chain reaction might produce mostly Caro's acid at 240 K.

The ratio of the yield of Caro's acid to sulfate produced by reaction (R1) is given by

\[
\frac{[\text{H}_2\text{SO}_4]}{[\text{H}_2\text{SO}_4]} = \frac{k_{13b}[\text{SO}_3^2^-]}{k_{13a}[\text{O}_2]} \tag{5}
\]

If reaction (R24) is the major chain termination reaction, the resulting steady state [\( \text{SO}_3^2^- \)] is

\[
[\text{SO}_3^2^-] = \frac{\sqrt{\phi}}{2k_{24}} \tag{6}
\]

At 240 K this yields [\( \text{SO}_3^2^- \)] \( \approx 6.0 \times 10^{-8} \) M and \( [\text{H}_2\text{SO}_4]/[\text{H}_2\text{SO}_4] \approx 1.0 \). Thus up to one third of the alkalinity could be converted to Caro's acid. Since the calculated [\( \text{SO}_3^2^- \)] is smaller than [\( \text{O}_2^* \)], reaction (R25) is the dominant sink if it has a rate constant that is comparable to or larger than that of reaction (R24). Unfortunately, the rate constant for reaction (R25) has not been measured.

The Caro's acid produced by reaction (R13b) will not necessarily oxidize halide ions. Caro's acid is also known to oxidize S(IV) via

\[
\text{HSO}_5^- + \text{SO}_3^2^- \rightarrow \text{H}^+ + 2 \text{SO}_4^{2-}. \tag{R4}
\]

This reaction is faster than (R3) and, at pH=7 the concentrations of \( \text{SO}_3^2^- \) and Br are comparable. However, once the pH drops, reaction (R4) ceases to be effective; furthermore the corresponding reaction with \( \text{HSO}_5^- \) is much slower [Betterton and Hoffman, 1988]. To evaluate the effect of (R4), we must compare the lifetime of \( \text{HSO}_5^- \) to the lifetime of \( \text{SO}_3^2^- \),

\[
\tau(\text{HSO}_5^-) = \frac{1}{k_{12}[\text{SO}_3^2^-]} \tag{7}
\]

\[
\tau(\text{SO}_3^2^-) < \frac{1}{k_{13a}[\text{SO}_3^2^-]} \tag{8}
\]

For the conditions assumed here, these lifetimes are 11 and 12 s, respectively. Reaction with \( \text{O}_2 \) makes the latter lifetime smaller. Thus although a significant fraction of the Caro's acid should react by (R4), a large part of the alkalinity could still be in the form of Caro's acid at the time the pH drops. Since \( A = 2.8[\text{Br}] \) and because of reaction (R6), less than 20% of the alkalinity needs to be converted to Caro's acid in order to release all the Br from the drop.

At 240 K with [\( \text{Br} \)] = 4.7x10^3 M, the lifetime of Caro's acid is 4.2 hours; this is much shorter than the particle lifetime. The characteristic times for the HOBr produced are (in milliseconds) for liquid phase diffusion (Appendix B), 0.7; gas phase diffusion, 0.09; chemical reaction (R6), 0.04. Thus the rate of escape from the drop is determined by the rate of liquid phase diffusion and most of the HOBr oxidizes Br instead of escaping from the drop.
Models of Arctic ozone depletion [McConnell et al., 1992; Fan and Jacob, 1992] show concentrations of BrO up to 30 ppt. In solution, BrO is thermodynamically capable of oxidizing SO$_3^-$ [Stanbury, 1989].

$$\text{BrO} + \text{SO}_3^- \rightarrow \text{BrO}^- + \text{SO}_2^- \quad \text{(R21)}$$

If this reaction proceeds at a fast enough rate to compete with reevaporation of BrO, then it should greatly enhance the production of Caro's acid and potentially cause the release of Br from the aerosol to be autocatalytic.

Another potential means of initiating the chain reaction is the oxidation of SO$_3^-$ by NO$_2$. Although the mechanism of this reaction is unknown, the electron transfer reaction (R22) is thermodynamically possible [Stanbury, 1989]. With [SO$_3^-$] = $A/2$, the lifetime of liquid phase NO$_2$ with respect to this reaction is $t_R = 12 \mu$s. Since this is much smaller than the characteristic lifetime of the liquid phase diffusion, $t_L = 700 \mu$s, the rate is controlled by the characteristic time for combined reaction and diffusion [Schwarz, 1986]; this is $(5t_{RT}A^2)^{1/2} = 120 \mu$s. Because of the low solubility of NO$_2$ the characteristic time for gas phase diffusion from the drop is only 0.10 $\mu$s; thus the surface of the drop is in equilibrium with gas phase NO$_2$. With a gas phase NO$_2$ mixing ratio of 30 ppt, reaction (R22) initiates $2\%$ as many chains as 1 ppt of HO$_2$. Thus this reaction is not significant after sunrise.

However, reaction (R22) may be important as a dark reaction. Because the chain termination is second order, the rate of free radical oxidation goes as the square root of the rate of initiation. Before sunrise, with NO$_2$ as the only significant gas phase radical, the rate of Caro's acid production is one seventh of that estimated above for HO$_2$ on the basis of equation (5). This is sufficient to release about $40\%$ of the initial Br. As a result, a reservoir of gas phase Br could accumulate before polar sunrise. Some HO$_2$ may be present at night because of the reaction of O$_3$ with olefins; $5 \times 10^5$ molecules cm$^{-3}$ of HO$_2$ are required to equal reaction (R22) in initiating free radical chains.

Another possible source of liquid phase radicals is the reaction of O$_3$ with H$_2$O$_2$ (R10). If the particles are in equilibrium with the gas phase, the ratio of radical production from reaction (R10) to that from reaction (R11) is

$$\frac{2k_{10}H_{2O_{2}}K_{17}P_{H_{2O_{2}}}}{k_{11}H_{2O_{2}}K_{16}P_{H_{2O_{2}}}} = 4.5 \times 10^{-10} \frac{P_{H_{2O_{2}}}}{P_{H_{2O_{2}}}} \quad \text{(9)}$$

Mass transfer effects increase this ratio by about a factor of 400; nevertheless, reaction (R10) is insignificant in comparison to reaction (R11), even in the dark.

The production of Caro's acid is much less efficient at higher temperatures. First, higher temperatures reduce the solubility of O$_3$ and therefore increase the lifetime of O$_3$. For example, at 298 K with 40 ppb of ozone the lifetime of O$_3$ with respect to reaction (R11) is 1.3 s. The longer lifetime and reduced solubility of HO$_2$ increase the likelihood of HO$_2$ reevaporation from the drop. [O$_3$] and therefore the effect of reactions (R26) and (R25) also increase. At 298 K, with 20 ppt of HO$_2$ as might be encountered in the marine boundary layer, reaction (R11) gives a steady state [O$_3$] of $3.0 \times 10^5$ M. At pH 7 the resulting lifetime of O$_3$ with respect to reaction (R26) is then just 33 ms; thus this becomes the dominant sink. As a result, only about 15% of the HO$_2$ radicals arriving at the drop are converted to OH and the rate of initiation of radical chains is only about a factor of 2 larger than with 1 ppt of HO$_2$ at 240 K. Furthermore, the efficiency of chain propagation is reduced at higher temperatures because of reduced solubility of SO$_3$. Thus the rate of Caro's acid production by reaction (R13b) is not changed very much by increased temperature. However, the large temperature dependences of reactions (R13a) and (R1) result in a faster rate of SO$_3^-$ production and therefore a smaller yield of Caro's acid. In addition, the loss of Caro's acid by means of reaction (R4) is greater at higher temperatures. During the Arctic summer, SO$_3^-$ is much lower than in winter; this further reduces the efficiency of the chain reaction. As a result this mechanism is probably not important in either the Arctic summer or the global marine boundary layer.

### Release of Bromine by Free Radical Reactions

When the alkalinity is fully converted to sulfate, the pH drops sharply. The calculations in the previous section indicate that the Caro's acid produced during the high pH interval may or may not be sufficient to oxidize all the sea-salt Br. Under moderate pH conditions, Br may be produced by radical-radical reactions in solution.

The OH radical has an extremely short lifetime in sea-salt solutions because it reacts rapidly with halide ions. This proceeds via HOX$^\cdot$ radicals (equilibria E20 and E21). For HOCl$^\cdot$, the acid-catalyzed reaction (R16) dominates over unimolecular dissociation for pH less than about 9; for HOBr$^\cdot$, the unimolecular reaction (R14) dominates above pH 4. At 298 K the equilibrium amounts of HOBr and HOCl$^\cdot$ in sea-salt solutions are roughly equal. Since the diffusion-controlled rate constants for (R16) and (R15) are virtually identical, roughly equal amounts of CI and Br form if the pH is below 4. Above this pH, production of Br dominates, as discussed by Zafiriou [1974]. At low temperatures, HOBr$^\cdot$ is favored and the formation of Br predominates over Cl$^-$ for all pH even if reaction (R14) is very slow. Of course, depletion of Br from the particle eventually causes the formation of Cl$^-$ to be favored.

Halogen atoms are rapidly converted to dihalogen radicals by equilibria (E22) and (E23). Both Cl$_2$ and Br$_2$ rapidly oxidize S(IV) [Shouete et al., 1991]. However, at low pH, where S(IV) concentrations are low, radical-radical reactions may predominate. Although Br$_2$ oxidizes superoxide

$$\text{Br}_2^\cdot + \text{O}_2^- \rightarrow 2 \text{Br} + \text{O}_2^\cdot \quad \text{(R27)}$$

it reduces HO$_2$

$$\text{Br}_2^\cdot + \text{HO}_2 \rightarrow \text{Br}_2 + \text{HO}_2^\cdot \quad \text{(R28)}$$

This may liberate Br$_2$ from sea-salt. In contrast, Cl$_2^\cdot$ oxidizes both O$_2^\cdot$ and HO$_2^\cdot$. These reactions prevent the buildup of Cl$_2^\cdot$ or Br$_2^\cdot$ to levels where significant halogen molecule production can result from self-reaction.
Both the rate constant and products of reaction (R28) have been questioned by Wagner and Strehlow [1987]. However, other rate constants resulting from their experiments are inconsistent with established values. This may be due to their neglect of the reaction of HO$_2$ with Br$_2$ in the complex mechanism used to fit the rate constants; if so, Wagner and Strehlow's conclusions on reaction (R28) are probably not valid.

To evaluate the production of Br$_2$ by reaction (R28), we need an estimate of the $\Phi$. At 240 K in the presence of 50 ppt of H$_2$O$_2$, the dominant S(IV) oxidation reaction is (R9) if the pH is below 5.9. Eventually, a steady state pH is established with the production of acidity by S(IV) oxidation being balanced by the evaporation of HCl from the drop:

$$\text{H}^+ + \text{Cl}^- \rightarrow \text{HCl}(g).$$

(R29)

The rate constant, $k_{HCl}$, for (R29) can be obtained from the requirement that at equilibrium the fluxes of HCl to and from the drop must be equal. If the drop radius is $a$ and the gas phase diffusion coefficient is $D_{HCl}$ we have for the rate constant of reaction (R29)

$$k_{HCl} = \frac{3D_{HCl}}{2aRTk_b}$$

(10)

Setting the rate of reaction (R29) equal to twice the rate of S(IV) oxidation, we obtain a steady state pH of 3.3 for the conditions considered here. Uptake of HNO$_3$ will lower the pH and increase the rate of Br$_2$ production estimated in the following. However, particle NO$_3^-$ is much lower than particle SO$_4^{2-}$ during the Arctic winter and spring [Bottenheim et al., 1990].

At 240 K with 1 ppt of HO$_2$ and 40 ppb of O$_3$, the major aqueous phase sink of HO$_2$ is reaction (R26) rather than (R11) if the pH is less than 5.8. Reaction (R26) is faster than reevaporation for pH greater than 2.9. Treating (R26) as the sole HO$_2$ sink, at steady state we have

$$[O_2^+] = \left(\frac{\phi k_{16}}{2k_{26}[H^+]}\right)^{1/2}$$

(11)

with $\phi$ given by equation (3). At pH 3.3 this yields $[O_2^+] = 2 \times 10^{-8}$ M. The rate of Br$_2$ formation is equal to the rate of reaction (R11) times the branching ratio between reactions (R27) and (R28). Thus

$$\frac{d[Br_2]}{dt} = k_{11}[O_2^-][H^+] - \frac{k_{28}[H^+]}{k_{28}[H^+] + k_{16}}.$$

(12)

This rate is a maximum at pH 4.5, independent of $\phi$ and O$_3$. At pH 3.3 this rate is about $4 \times 10^{-8}$ M s$^{-1}$ and all the Br in a sea-salt particle could be oxidized in about 16 hours. At pH 4.5 this rate is $1 \times 10^{-7}$ M s$^{-1}$ and the Br could be oxidized in about 6 hours.

Some of the Br released is converted to HBr and should return to the particle phase. Most of the HBr condenses on the highly acidic fine sulfate particles since these have most of the aerosol surface area [Suebler et al., 1994]. Li et al. [1990] have observed that most of the particulate Br is in the fine sulfate particles. At the very low pH of the sulfate particles, this mechanism is insignificant.

Under global marine boundary layer conditions (298 K, 20 ppt H$_2$O$_2$, 20 ppb O$_3$, 50 ppt SO$_2$) the pH is controlled by the balance between (R29) and (R11); this gives a steady state pH of 6.4. Under these conditions, equation (10) is valid for pH between 3.9 and 9.2; this yields $[O_2^+] = 2 \times 10^{-4}$ M. However, the rate of production of Br$_2$ is much less than the rate of reaction (R11) due to the competition between (R27) and (R28). The resulting Br$_2$ formation rate is $1 \times 10^{-8}$ Ms$^{-1}$ so that the Br lifetime is about 60 hours. Additional acidification of the particles by HNO$_3$ uptake increases the Br$_2$ formation rate according to equations (10) and (11). The maximum Br$_2$ production rate at pH 4.5 gives a Br lifetime of 12 hours. Rancher and Kritz [1980] have reported that a large fraction of the particulate sea-salt Br is converted to gas phase inorganic Br in the course of 1 day.

**Autocatalytic Release of Halogens**

In addition to these primary release mechanisms, there are possible autocatalytic cycles for the release of bromine from sea-salt. Gas phase Br atoms are converted into BrO via

$$Br + O_3 \rightarrow BrO + O_2.$$  

(R30)

As noted above, BrO radicals may initiate free radical reactions in the particle phase. Also, gas phase Br is converted into either HBr by reaction with hydrocarbons or HOBr via

$$BrO + HO_2 \rightarrow HOBr + O_2.$$  

(R31)

If HOBr returns to the sea-salt particles, it can oxidize Br to Br$_2$, via reaction (R6). This reaction may also occur on suspended ice crystals or on the snowpack; the corresponding reaction with Cl has been observed [Abbatt and Molina, 1992]. The result is the conversion of one active Br (HOBr) into two active Br atoms (Br$_2$). If more than half the Br atoms released are converted to HOBr, this results in an amplification of the photochemically active Br in the air mass. If the production of HBr exceeds HOBr, then not all the HBr is recycled and Br gradually accumulates in this inactive form unless there is another means of recycling HBr. Although the primary Br$_2$ production mechanisms are relatively slow, they may be important in maintaining active Br levels if the yield of HOBr is slightly less than the yield of HBr.

Processes that favor the production of HBr instead of HOBr are the conversion of BrO back to Br atoms

$$BrO + BrO \rightarrow 2Br + O_2,$$  

(R32)

or

$$BrO + NO \rightarrow Br + NO_2.$$  

(R33)
and the photolysis of HOBr

\[
\text{HOBr} + h\nu \rightarrow \text{Br} + \text{OH}.
\]  
(R34)

These reactions are essential parts of the catalytic cycle that destroys \(O_3\). If reaction (R6) is the main means of recycling active Br, then the efficiency of the recycling should be very sensitive to the details of the gas phase chemistry.

Reactions (R32) and (R34) are much slower for chlorine than for bromine, as a result the autocatalytic cycle should be much more efficient for Cl. Also, in the marine troposphere there is much more \(O_3\) than in the Arctic. This favors the production of HOCl and therefore shifts the cycle toward the autocatalytic mode. In the global marine atmosphere, where the primary reactions discussed here are not very efficient, these cycles may be critical to the formation of significant active Cl concentrations. Evidence that significant active Cl is produced in the marine boundary layer has been given by Keene et al. [1990] and Puxxeney et al. [1993]. However, the rate of Cl release by reaction (R5) is less than the rate of release by (R29). At 273 K about 2 ppb of HOCI(g) is needed for (R5) to release Cl as fast as (R29), while at 298 K over 50 ppb of HOCI is needed. Thus this mechanism does not explain the high rate of Cl release from sea-salt.

**Conclusions**

Under conditions encountered during polar sunrise, bromine molecules may be released from sea-salt aerosol particles on a timescale of a few hours by either the production of Caro's acid in the free radical oxidation of \(S(IV)\) at high \(pH\) or the direct free radical oxidation of bromide at moderate \(pH\). These mechanisms are capable of converting virtually all the sea-salt bromide into gas phase bromine. The former mechanism requires both low temperature and high \(SO_2\) concentrations; as a result it causes \(Br_2\) release only during the winter and early spring, as is observed. The latter mechanism could oxidize significant amounts of sea-salt Br in the global marine boundary layer. HOCl and Cl are only minor products of these reactions.

The evaluation of these mechanisms at low temperatures is very uncertain because of incomplete physical-chemical data. In particular, the yield of Caro's acid depends critically on the temperature dependence of the rate constant and branching ratio of the free radical oxidation of \(S(IV)\) via reactions (R13a) and (R13b). In addition, data are needed on the mechanism and temperature dependencies of reaction (R22), the possible occurrence of reactions (R20) and (R25), and the effect of ionic strength on these rate constants.

In addition to the primary release mechanisms, there are possible autocatalytic cycles that may enhance the release of bromine from sea-salt once some active bromine is formed. These are the initiation of liquid phase free radical chemistry by BrO supplied from the gas phase and the oxidation of bromide ions to elemental bromine by HOBr supplied from the gas phase. Evaluation of these processes will require coupling the appropriate liquid phase chemistry to a detailed model of the gas phase chemistry.

**Appendix A: Estimates of Temperature Dependencies**

Many of the equilibrium and rate constants used here have only been measured near room temperature. To estimate temperature dependencies, it is much better to use estimates of entropy changes rather than enthalpy changes; this is because entropies usually vary in a more systematic and predictable manner than enthalpies. Thus most of these estimates are made by estimating \(\Delta S\) and then determining the value of \(\Delta H\) required to give the correct rate or equilibrium constant at the temperature of measurement.

To estimate temperature dependencies for gas solubilities, entropies of solution were estimated by the method of Berdnikov and Bachin [1970]. The solubilities of HOCI, HOBr, Cl\(_2\), and Br\(_2\) were calculated from thermodynamic data tabulated by Wagner et al. [1982] and by Benson [1976] (for HOBr(g)). The origin and reliability of these data are not clear; in particular the quoted uncertainty (±2 kcal mol\(^{-1}\)) in \(\Delta H_f^\circ\) for HOBr(g) leads to a factor of 30 uncertainty in the solubility. The resulting HOBr solubility is only a little larger than the solubilities of Br and Br\(_2\); this amounts to assuming that HOBr is almost entirely nonpolar, with very little tendency to hydrogen bond with water. The larger solubility of HOCI must be due to hydrogen bonding; this should be less effective for HOBr since the OH bond is less polar, as indicated by the fact that HOBr is a weaker acid than HOCI. Even the upper limit to the solubility of HOBr is smaller than the solubility of HOCI. The calculated solubilities of HOCI are consistent with the experimental estimates of Hanson and Ravishankara [1991] for \(H_2SO_4\) solutions.

For equilibria (E16) and (E17), temperature dependencies were obtained by using the observation that the entropies of dissociation of all noncharged acids are near \(-11R\) [Pitzer, 1937]. Equilibrium (E15) was assumed to have the same \(\Delta S\) as (E19).

Equilibria (E20) through (E23) all involve a neutral species combining with an ion to form an ion. From the arguments given by Pitzer [1937], we should expect reactant and product ions to have similar entropies of solution. If we consider a cycle consisting of removing the reactants to the gas phase, conducting the reaction in the gas phase, and returning the products to the solution, we see that \(\Delta S_p\) for the solution reaction should be nearly equal to \(\Delta S_p\) for the gas phase reaction minus the entropy of solution of the neutral species, \(\Delta S_o\). Let \(\Delta S_p\) be the entropy change for the reaction of the corresponding gas phase neutral species. Then \(\Delta S_p\) differs from \(\Delta S_o\) only by the difference in the electronic entropies of the ions and the neutral species. The halide ions and the neutral molecules corresponding to the products have electronic entropies of zero. The halogen atoms have \(S_e^0 = Rh_0^4\), from the \(P_{3s}\) ground state. The molecular ions have \(S_e^0 \approx Rh_0^2\), from spin. Therefore we have for all of these reactions

\[
\Delta S_p = \Delta S_o + 3Rh_2 - \Delta S_e
\]  
(A1)

Using data from Benson [1976] we have \(\Delta S_p/R\) equal to -13.5, -13.3, -12.9, and -12.6 for reactions (E20), (E21), (E22), and (E23), respectively. From Berdnikov and
Appendix B: Characteristic Time for Diffusion
From a Drop

The literature contains a variety of expressions for the characteristic time for liquid phase diffusion. There is no single, compelling way to define this for the reaction of a species entering a drop because the rate is never entirely controlled by liquid phase diffusion. However, if a species is produced uniformly throughout a drop at rate $S$ and escapes to the gas phase, there is a well defined liquid phase lifetime. This can be obtained by solving the steady state continuity equation

$$ S = -D_L \frac{\partial}{\partial r} (r^2 \frac{\partial [A]}{\partial r}) $$

subject to the boundary condition $[A]=0$ at the surface of the drop. This amounts to assuming that the escape from the drop is controlled only by liquid phase diffusion. The solution is

$$ [A] = \frac{S}{6D_L} (r^2 - r^2_0) $$

If we integrate over the volume of the drop to obtain the average concentration and divide by the production term, $S$, we obtain for the average lifetime

$$ \tau_{av} = \frac{a^2}{15D_L} $$

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References


MOZURKEWICH: RELEASE OF HALOGENS FROM SEA-SALT PARTICLES


Michael Mozurkewich, Department of Chemistry, York University, 4700 Keele Street, North York, Ontario M3J 1P3, Canada E-mail F5300530@SOL.YORKU.CA

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