Uptake of Hypobromous Acid (HOBr) by Aqueous Sulfuric Acid Solutions:

Low -Temperature Solubility and Reaction

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Abstract:

Hypobromous acid (HOBr) is a key species linking inorganic bromine to the chlorine and odd hydrogen chemical families. We have measured the solubility of HOBr in 45 - 70 wt% sulfuric acid solutions representative of upper tropospheric and lower stratospheric aerosol composition. Over the temperature range 201 - 252 K, HOBr is quite soluble in sulfuric acid, with an effective Henry's law coefficient, $H^* = 10^4 - 10^7$ mol L^{-1} atm^{-1}. H^* is inversely dependent on temperature, with $\Delta H = -46.2$ kJ mol^{-1} and $\Delta S = -106.2$ J mol^{-1} K^{-1} for 55 - 70 wt% H_2SO_4 solutions. Our study includes temperatures which overlap both previous measurements of HOBr solubility. For uptake into aqueous 45 wt% H_2SO_4, the solubility can be described by log $H^* = 3665/T - 10.63$. For 55 – 70 wt% H_2SO_4, log $H^* = 2412/T - 5.55$. At temperatures colder than ~ 213 K, the solubility of HOBr in 45 wt% H_2SO_4 is noticeably larger than in 70 wt% H_2SO_4. The solubility of HOBr in 45 wt% H_2SO_4 is comparable to that of HBr, indicating that upper tropospheric and lower stratospheric aerosols should contain equilibrium concentrations of HOBr which equal or exceed those of HBr. Our measurements indicate chemical reaction of HOBr upon uptake into aqueous sulfuric acid in the presence of other brominated gases followed by evolution of gaseous products including Br_2O and Br_2, particularly at 70 wt% H_2SO_4.

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1. Introduction

Halogen species are known to catalytically destroy ozone in many regions of the atmosphere. Bromine is the dominant halogen responsible for the near-total loss of ozone at ground level in high-latitude springtime events (Martinez et al., 1999), and it participates in approximately 25% of the stratospheric ozone depletion observed over Antarctica in the springtime (Albritton et al., 1994). In addition to direct catalytic losses, bromine compounds can indirectly enhance ozone loss through coupling to other radical families.

In the Arctic boundary layer, hypobromous acid (HOBr) is believed to play a significant role in Br activation during "Bromine Explosion" events (Fan and Jacob, 1992; Finlayson-Pitts and Pitts, 2000). Observations of *Foster et al.* (2001), who found higher levels of Br_2 in the snow pack than in the air above the surface, strongly support the occurrence of

$$HOBr + HBr \rightarrow Br_2 + H_2O \quad (1)$$

on snow pack surfaces in the Arctic. Reaction 1 has been studied at room temperature; *Beckwith et al.* (1996) examined the effect of ionic strength and found the forward reaction to be general acid catalyzed, involving Br$^+$ transfer to Br$^-$ as proton transfer occurs from the acid, HA, to HOBr. Wintertime Arctic haze events, which are dominated by acidic sulfate particles (Barrie and Barrie, 1990), are clearly a suitable environment for such aqueous phase conversion. In addition, autocatalytic reactions involving HOBr are the most likely source of elevated BrO observed over the Dead Sea (Matveev et al., 2001).

Higher in the atmosphere, *Murphy and Thompson* (2000) found that bromine was most commonly found in aerosols just above the tropopause, where particulate Br may represent a significant fraction of total inorganic Br. Strong evidence indicates that HOBr is the major stratospheric bromine reservoir before sunrise at high and mid-latitudes (Sinnhuber et al., 2002), suggesting that heterogeneous behavior of HOBr may be particularly important at night. Furthermore, since heterogeneous Br reactions are faster than corresponding Cl reactions at temperatures well above those needed to form polar stratospheric clouds (PSCs) (Meilinger et al., 2001), the aqueous-phase coupling reaction

$$HOBr + HCl \rightarrow BrCl + H_2O \quad (2)$$
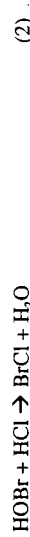
may provide a pathway for chlorine activation on sulfate aerosols at temperatures warmer than those required for PSC formation (Michelsen et al., 1999; Danilin and McConnell, 1995; Lary et al., 1996), potentially leading to chlorine activation earlier in the season or over an expanded geographical area. This pathway could be especially important under conditions where chlorine

processing is incomplete, such as at the polar vortex edge, or in warmer arctic winters. Perhaps most importantly, as the stratosphere cools due to climate change processes, larger areas may have sufficiently cold temperatures for stratospheric chlorine activation via coupling with bromine on sulfate aerosols.

Clearly it is important to understand the multiphase behavior of HOBr under atmospherically relevant conditions. Here we present measurements of HOBr solubility in low-temperature aqueous sulfuric acid (H_2SO_4) solutions representative of stratospheric sulfate aerosol particles. We also provide evidence for Br_2 and Br_2O production when HOBr and HBr interact in cold, acidic solution. Br_2 may be produced by Reaction 1; H_2SO_4 is a strong dehydrating agent, and thus production of dibromine monoxide is not unexpected:

$$HOBr + HOBr \rightarrow Br_2O + H_2O. \qquad (3)$$
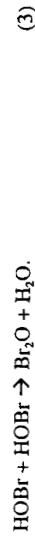
2. Experimental

The time-dependent uptake technique used for the measurements reported here has been described in detail elsewhere (Finlayson-Pitts and Pitts, 2000; Klassen et al., 1999; Iraci et al., 2002). The Knudsen cell consists of two Teflon-coated Pyrex chambers separated by a valve, with the aqueous sulfuric acid sample placed in the bottom chamber and cooled by immersion in an alcohol bath. Gaseous HOBr and water are introduced separately into the top chamber, which has a small aperture leading to a differentially pumped mass spectrometric detection system (Balzers QMG 421 quadrupole mass spectrometer with electron ionization). The concentration in the top chamber is kept below 25 mTorr, and the residence time in the top chamber is determined by the size of the escape aperture. The five warmest experiments on 45 wt% H_2SO_4 had vapor pressures higher than 25 mTorr, but even under those conditions, the mean free path was never less than radius of escape aperture; this requirement established the upper temperature limit for exposure of HOBr to the most dilute acid solution. When the valve between the two chambers is opened, loss of the gas-phase species to the surface competes with escape through the aperture and is observed as a decrease in the mass spectrometer signal. The net uptake coefficient, γ, is defined as the fraction of incident molecules which is lost to the surface.

The number of HOBr molecules lost to the surface is measured by the change in flow through the escape aperture upon exposing the sample. The number of HOBr molecules lost to the surface is measured by the change in flow through the escape aperture before and after exposing the sample. The refer to the gas flow rate out of the Knudsen cell before and after exposing the sample. The number of gas-surface collisions per second is derived from gas kinetic theory as $\bar{c}nA_s/4$, where

$\bar{c}$ is the average molecular velocity (cm s^{-1}), n is the density of gas molecules (molecules cm^{-3}), and A_s is the area of the reactive surface (cm^2). The gas density, n, is determined by the flow into the Knudsen cell and the rate of "collision" with the escape aperture, $n = 4\,F/\bar{c}A_h$, where A_h is the area of the aperture (cm^2). Thus, in terms of the Knudsen cell parameters

$$\gamma = \frac{A_h}{A_s}\frac{F_o - F}{F} \qquad (4)$$

In its current configuration, the cell can be operated with one of two aperture areas, 0.049 cm^2 or 0.018 cm^2, and the sulfuric acid has a surface area of 5.7 cm^2. Because the MS signal is linear with flow, the signals are used directly in Eq. 4.

The solubility of a species is measured by observing the time dependence of the uptake coefficient. The solute enters the sulfuric acid at a rate determined by liquid-phase diffusion away from the surface and by its solubility and reaction in sulfuric acid. As the HOBr concentration increases in the sulfuric acid, the net uptake coefficient, which represents the difference between sticking and evaporation, decreases. The equation describing the time-dependence of the uptake coefficient is

$$\frac{1}{\gamma(t)} = \beta + \left[\frac{4RTH^*}{\bar{c}} \left(\sqrt{\frac{D}{\pi t}} + \sqrt{Dk} \right) \right]^{-1} \qquad (5)$$

where R (L atm mol^{-1} K^{-1}) is the gas constant, T (K) is the temperature of the gas, H^* (M atm^{-1}) is the Henry's law solubility, k is the rate coefficient describing any pseudo-first-order reaction which may occur, and D (cm^2 s^{-1}) is the liquid-phase diffusion coefficient. (Finlayson-Pitts and Pitts, 2000; Hanson and Ravishankara, 1993; Worsnop et al., 1989). β is an intercept term which includes gas-phase diffusion and accommodation limitations, if any; in the usual notation, $\beta = \Gamma_g^{-1} + \alpha^{-1}$. In the absence of reaction, the quantity $H^*\sqrt{D}$ is determined from the reciprocal of the slope of a plot of $1/\gamma(t)$ versus $\sqrt{(t)}$. To determine H^*, the liquid-phase diffusion coefficient is calculated from the equation $D = c \times T/\eta$, where c (cm^2 cP s^{-1} K^{-1}) is a constant that depends on the solvent and on the diffusing species, T (K) is the temperature of the liquid, and η (cP) is the viscosity of the liquid. For HOBr in sulfuric acid, c is estimated as 6.2×10^{-8} cm^2 cP/s K using the approach of Klassen et al. (1998). The sulfuric acid viscosities are calculated from the equations in Willinas and Long (1995).

Hypobromous acid (HOBr) is thermally and photolytically unstable, thus it must be prepared shortly before use. Several methods are reported in the literature, and we have used a method that

allows some purification of the product mixture before its use. Silver nitrate (25 g) is dissolved in water (150 mL) and reacted with excess Br_2 (5 mL). The HOBr produced is collected by vacuum distillation into 30 wt% H_2SO_4, held at -40°C. After several attempts, we have devised a preparatory scheme that delivers an adequate supply of gas phase HOBr from this acidic solution to our Knudsen cell apparatus. In brief, a portion of the collected solution is transferred to a bubbler and acidified further to enhance the vapor pressure of HOBr over the solution. Then the sample is bubbled with helium to remove much of the excess Br_2 collected during the distillation. After the solution color has changed from orange to yellow (indicating the removal of the majority of the Br_2), the bubbler is placed in a dry ice/isopropanol bath. Helium, nitrogen, and other gaseous impurities are pumped off, and the bubbler is allowed to thaw in ice water. Once melted, the vapor over this solution is introduced to the Knudsen cell using only Teflon tubing and fittings. The bubbler is kept in the dark in an ice-water bath during use and can be stored at ~0°C in the dark for nearly a week.

The two major isotopes of HOBr were detected mass spectrometrically at m/z = 96 and 98. Also present in the gas stream were large amounts of water vapor (m/z = 18) and several other brominated gases. Br_2^+ (m/z = 160) was detected in significant quantities and was greatly reduced by bubbling with helium at the start of each day. Through the course of a day, however, some Br_2 did regenerate in solution. Also, Br_2O^+ (176) and HBr^+ (80) were also present and varied in relative amount from one batch of HOBr to the next. In general, the signal from Br_2 was comparable to that of HOBr, Br_2O was roughly 10% of the signal from HOBr, and HBr was usually 2-5 times higher than HOBr. Due to the mixture of gases in the HOBr stream and the dominance of water, only a rough estimate of the HOBr partial pressures can be made. Assuming an equal mass spectral response from both HBr and HOBr, comparison of HOBr signals to those of pure HBr in test experiments suggests that HOBr levels were on the order of 2×10^{-5} Torr in the Knudsen cell. Furthermore, flow conditions were varied from experiment to experiment, with the range of HOBr partial pressures spanning perhaps 1×10^{-5} - 2×10^{-4} Torr over the suite of exposure experiments discussed below. Additional water was introduced to maintain the vapor pressure of water over the sulfuric acid solution at the experimental temperature, thus preventing evaporation and changes to the composition of the acid. Water pressures often matched the vapor pressure to within 10%, and most were better than 60%. Occasionally, difficulties in setting flow rates led to differences of 100% or more.

In the presence of so much water vapor, we cannot rule out the possibility of reactions on wet wall surfaces. To test for changes in HOBr flow due to additional small surface area once the valve was opened, we performed blank exposures on the empty reactor at room temp and colder. Sometimes we saw very small indications of uptake, much smaller than the uptake due to solubility. Sometimes we saw a transient passivation effect; upon initial exposure HOBr and Br_2O were lost to the walls, with possible indications of Br_2 production. After just a moment or two of exposure, this effect was no longer present. Each morning, before starting a series of experiments, we flowed the reactant gas stream through the upper, larger portion of the reactor to passivate the wall surfaces. We did not passivate the lower chamber in the presence of sulfuric acid samples, but no difference was seen between measurements made early in the day and those made later on in the series, indicating that the quantity of HOBr lost to "fresh" walls beneath the valve was negligible.

Temperatures were measured with several K-type thermocouples attached to the outside of the glass cell. One was located at the level of the meniscus, which gave the most reliable results and were used almost exclusively. Temperatures were recorded to 0.1 K and were calibrated via comparison to the water vapor pressure measurements of Zhang et al. (1993). To do so, a Baratron capacitance manometer was zeroed with the cell evacuated, and then the vapor pressure over the known H_2SO_4/H_2O solution was measured. The parameterization of Zhang et al. was used to predict the temperature for the observed vapor pressure, and the thermocouple readings were adjusted to match. This adjustment was always ≤ 3 K, and often ≤ 1 K. The last step in determining the temperature of an uptake measurement was to account for drift during an experiment. The coolant bath was stirred between experiments, but due to coupling with the stir bar in the acid solution, stirring had to be halted during exposure. Thus, the temperature of the bath and the solution drifted. For most experiments, the drift was less than 1 K, but for the coldest experiments, a drift of up to 2 K was experienced. The temperatures reported here are the average of the warmest and coldest during the exposure, and are not expected to be better than ± 0.5 K overall.

Sulfuric acid solutions were prepared from concentrated H_2SO_4 (Mallinckrodt) and deionized (Millipore) water. Titrations with standard NaOH solutions identified the acid solutions used here as: 70.1 ± 0.5, 60.7 ± 0.5, 55.2 ± 0.6, 45.3 ± 0.4, and 43.6 ± 0.2 wt% H_2SO_4. Solubility measurements on the 45.3 and 43.6 wt% solutions are reported collectively below as "45 wt%."

3. Results & Discussion

Uptake on aqueous 45 wt% H_2SO_4 solutions

As shown in Figure 1, the uptake of HOBr on 45 wt% H_2SO_4 solutions demonstrated the time-dependent behavior of simple solubility. Panel 1a shows the mass spectrometer signal at m/z = 98 ($HO^{81}Br$) as a function of time. Exposure to the acid solution was begun at t = 0 s and terminated at t = 400 s. Panel 1b shows the inverse of the calculated uptake coefficient, γ, (Eq. 4) as a function of the square root of exposure time. The linear result is indicative of solubility-driven uptake (k = 0 in Eq. 5). For this example (45.3 wt% H_2SO_4, 219.0 K), the determined Henry's law coefficient was 6.3×10^5 M atm^{-1}. At significantly colder temperatures (201.5 K, not shown), a value of 2.2×10^7 M atm^{-1} was found. For several experiments, the values were confirmed by comparison to the lighter isotope, $HO^{79}Br$, which usually agreed within 15%. Results for individual experiments are reported in Table S1, which can be found in the Supplemental Information.

Over thirty experiments were performed on 45 wt% H_2SO_4 and were grouped into 1 K temperature bins. The average value of $H*$ in each bin is shown by the green circles in Figure 2. Individual values within a bin were often in excellent agreement, and most bins contained values which agreed within a factor of two. Those with the most measurements sometimes had a spread as large as a factor of four. Also shown in Figure 2 as the blue solid line is the extrapolated (hypothetical) solubility of HOBr in water. The 298 K lower limit estimate of ~1900 M atm^{-1} (Sander, 1998; Blatchley et al., 1992) was combined with the temperature dependence of HOCl (Huthwelker et al., 1995) as a best approximation.

As expected, HOBr is more soluble in colder acid solutions. From the slope of the best fit line (log $H* = 3665/T - 10.63$, solid green line), the enthalpy of solution is determined to be -70.2 kJ mol^{-1}, and the entropy is -203.5 J mol^{-1} K^{-1}. The latter indicates that during condensation and dissolution, HOBr loses significantly more entropy than would be expected for simple condensation (~ -85 J mol^{-1} K^{-1} from Trouton's Rule) or normal solvation, ~ -125 J mol^{-1} K^{-1} (ref?); suggesting considerable ordering of the solvent around the solute. This is consistent with the large negative enthalpy observed as well.

Other mass-to-charge ratios were also monitored during exposure, and behavior of the HBr (m/z = 80), Br_2 (160), and Br_2O (176) impurities could be observed. All three trace gases showed uptake into 45 wt% H_2SO_4 solutions at all temperatures studied for 45 wt% H_2SO_4 (201.5 - 237.9 K).

Uptake on aqueous 70 wt% H_2SO_4 solutions

Uptake of HOBr onto 70 wt% H_2SO_4 solutions often resulted in behavior different than that for uptake onto 45 wt% solutions. Many observations were similar to those shown in Figure 3, but at colder temperatures, results such as that shown in Figure 1b, where negative deviation from the expected linear behavior indicates slower solution saturation, suggesting additional uptake processes are contributing beyond simple solubility. This enhanced uptake response was observed for most experiments at temperatures < 224 K and suggests a reactive process is also contributing to the uptake.

As discussed above, solution-phase reactions of HOBr with itself and with HBr are known. For experiments which showed enhanced uptake, we searched for gaseous products. The mass spectrometer signals at m/z = 160 (Br_2) and 176 (Br_2O) during two types of experiments are shown in Figure 4. In panel 4b, the signals for Br_2 and Br_2O were monitored during the experiment shown in Figure 3. Initially, both species are present as impurities in the HOBr flow. Once exposure begins, Br_2 and Br_2O are generated in solution and released to the gas phase, increasing the mass spectrometer signal. When exposure stops near 800 s, both gases return to their previous levels. This behavior was seen only with 70 wt% H_2SO_4 solutions, and then most commonly in the colder temperature regime ($\leq$ 228 K). Production of Br_2O was seen in all 70 wt% experiments with $T \leq$ 228 K; Br_2 was also released from solution in nearly all of these experiments. For comparison, Figure 4a shows the behavior of Br_2 and Br_2O during the exposure of HOBr (and impurities) to 45 wt% H_2SO_4 shown in Figure 1. For clarity, the Br_2O signal has been magnified by a factor of 2.5. When exposed to 45 wt% H_2SO_4, it is obvious that Br_2 and Br_2O are both taken up by the solution.

Why is reaction only clearly observed for exposure of HOBr to 70 wt% H_2SO_4 solutions with $T \leq$ 228 K? An answer can be found by analogy in the case of HOBr + HCl, as measured by *Waschewsky and Abbatt* (1999) as a function of both temperature and wt% H_2SO_4. Those authors found that the second-order rate constant increased with acidity at each temperature studied and that the temperature effect was least pronounced in 70 wt% solution. Thus, we are observing an increase in reaction rate with increased acidity (due to increased k) and with decreased temperature (due to increased solubility).

Due to the competing reactions of HOBr in the 70 wt% H_2SO_4 system, the Henry's law coefficient must be extracted from a three-parameter ($H*$, k, and β) fit of Eq. 5 to the data, once again calculating diffusion constants as described by *Klassen et al.* (1998). For the example K).

shown in Figure 3 (70.1 wt% H_2SO_4, $T = 211.9$ K), $H* = 4.3 \times 10^5$ M atm⁻¹. Please see the Appendix for a brief discussion of the non-linear fitting procedure.

Values of $H*$ extracted from a three-parameter fit agreed very well with those from a linear fit for 45 wt% solutions and for 70 wt% solutions where the parameter k was found to be small. For significant values of k, such as in the example shown in Figure 3, the $H*$ value determined from the three-parameter fit was a factor of 3 - 10 lower than the value determined from a linear fit through a somewhat arbitrary, early portion of the data. Fitting the full equation (Eq. 5) was less susceptible to human influence and thus was trusted as a method less prone to error. The values reported throughout this manuscript are those determined from three-parameter fits of entire data sets; in many cases, $k = 0$.

Experiments were performed over the range of 211.9 - 251.6 K, resulting in nearly forty determinations of $H*$ in 70 wt% H_2SO_4 as a function of temperature. These results were averaged in 1 K bins and are shown as the solid squares in Figure 2. Once again, the solubility of HOBr is inversely dependent on temperature, but with a different slope than that seen for 45 wt% H_2SO_4 solutions (log $H* = 2453/T - 5.73$, not shown). These parameters result in values of $\Delta H = -47.0$ kJ mol⁻¹ and $\Delta S = -109.6$ J mol⁻¹ K⁻¹. At temperatures colder than ~ 213 K, the solubility of HOBr in 45 wt% H_2SO_4 is noticeably larger than in 70 wt% H_2SO_4.

The fitting parameter k represents the additional loss of HOBr due to reaction in 70 wt% H_2SO_4 solution. Its value increases with decreasing temperature (log $k = 2112.3/T - 12.0$ in 1 K bins), suggesting that k is driven by the solubility of the reaction partner, rather than by the rate constant of the elementary reaction. The temperature dependence of k very closely matches the temperature-dependent behavior of $H*$ for HBr in 70 wt% H_2SO_4 (slope = 2063.8, (Sander et al., 2003)), providing support for HOBr + HBr → Br_2 + H_2O as the dominant process which enhances uptake under these conditions. Because HOBr is ~15 times more soluble than HBr in 70 wt% H_2SO_4, our solutions should have contained 3-8-fold more HOBr than HBr. Thus, HBr is in excess and the fitting parameter k cannot be interpreted simply as a pseudo-first order rate coefficient. *Uptake on aqueous 55 and 60 wt% H_2SO_4 solutions*

Several solubility measurements were also made on 55 and 61 wt% H_2SO_4 solutions. These data indicated uptake due to simple solubility in most cases, with a few observations suggestive of reaction but not definitive. The solubility values are shown as 1 K averages in Figure 2. As reported by others (Waschewsky and Abbatt, 1999; Hanson, 2003), we do not observe a significant acidity dependence for solutions in this regime. In this respect, HOBr is quite different from HBr, which is approximately 4 orders of magnitude more soluble in 45 wt%

H_2SO_4 than in 70 wt% (Sander et al., 2003). A non-zero k parameter was occasionally found in the 55 and 60 wt% experiments, but no pattern or clear temperature trend was demonstrated.

All values for $H*$ in 55 - 70 wt% H_2SO_4 solution were averaged together in 1 K temperature intervals, and the least-squares fit is shown in Figure 2 as the solid black line (log $H* = (2412 \pm 290)/T - (5.55 \pm 1.30)$, where the quoted uncertainties are 1σ). From the slope of this line, an enthalpy of solvation of -46.2 kJ mol⁻¹ was determined ($\Delta S = -106.2$ J mol⁻¹ K⁻¹). For comparison, it is noted that for uptake of HBr into 66 wt% H_2SO_4, *Williams et al.* (1995) found $\Delta H = -42.3$ kJ mol⁻¹ indicating that our observed temperature dependence for HBr uptake into 55-70 wt% H_2SO_4 solutions is quite similar, despite significant differences in solute acidity. Furthermore, the present value of $\Delta H = -46.2$ kJ mol⁻¹ is midway between the two values currently available for HOBr: -52.3 kJ mol⁻¹ measured by *Hanson* (2003), and -38 kJ mol⁻¹ reported by *Waschewsky and Abbatt* (1999). Thus, our measurement closely confirms the averaged enthalpy of solvation (-45.2 kJ mol⁻¹) used by Hanson in his parameterization, which is shown as the dotted red line at warmer temperatures in Figure 2. The entropy value determined here for HOBr uptake into 55 - 70 wt% H_2SO_4 ($\Delta S = -106.2$ J mol⁻¹ K⁻¹) is comparable to that estimated by *Williams et al.* for HBr uptake (-113 J mol⁻¹ K⁻¹) and is slightly less negative than for methanol (-134 J mol⁻¹ K⁻¹ (Iraci et al., 2002)) and acetone (-172 J mol⁻¹ K⁻¹ (Klassen et al., 1999)) uptake into sulfuric acid solution.

Also shown in Figure 2 (dashed blue line) is the result of *Waschewsky and Abbatt* (*W&A*) (1999) from measurements conducted at 213-238 K; our results match theirs extremely well. The narrow gray lines show the standard error of the regression line through our data, where σ =

$$0.274 = \sqrt{(N-2)^{-1} \Sigma(y_{expt} - y_{fit})^2}.$$ Our study includes measurements which overlap the temperature regimes of both previous studies, and our results are considerably closer to those of *W&A*. *Hanson* attributes the difference between his values and those of *W&A* to differences in analysis method. The *W&A* technique requires an estimate of the liquid phase diffusion constant, as does the current measurement. Thus, our measurements could be argued to be low due to an inadequacy in calculating D. Previous studies in our apparatus (Iraci et al., 2002; Williams et al., 1995), however, have shown identical results for two different techniques, one requiring an estimate of D and one using an approach similar to that of *Hanson* (2003), i.e., a method which measures the equilibrium vapor pressure over a solution and requires no presumption about the liquid-phase diffusion constant. Thus, we feel confident using the time-dependent uptake technique presented here and believe the estimated values of D to be wholly adequate. Furthermore, to raise the present $H*$ values to meet those of *Hanson* (2003), $\sqrt{D}$ would need to

be lowered by a factor of 10, which implies our D values are incorrect by two orders of magnitude. Such an error seems highly unlikely, as D values have been directly measured for HBr and similar species in the acidity range considered here (Klassen et al., 1998). One possible explanation for the high solubility values reported by Hanson (2003) is uptake enhancement due to reaction with impurities in the HOBr source, such as those observed in the present work and discussed by Hanson (2003).

4. Implications

The solubility of HOBr in aqueous sulfuric acid solutions is significant, and the observed reactions producing volatile brominated gases ensure that uptake of HOBr into acidic aerosol particles will not saturate. Production of Br_2O, Br_2, and by analogy BrCl, will continue as long as source gases are available.

These reactions can be considered in three environments of potential interest: the Arctic troposphere, the contemporary lower stratosphere, and a future lower stratosphere affected by climate change. In the Arctic troposphere, where anthropogenic influence can lead to acidified sea salt aerosols, solution-phase reactions of HOBr must be considered. As previously explored (e.g., Vogt et al., 1996; Sander and Crutzen, 1996; Moldanova and Ljungstrom, 2001), the aqueous chemistry in such ionic systems is highly coupled. Thus, reaction of HOBr with HCl may initially produce BrCl, but the fate of that molecule depends on the concentration of Br^- in solution. Thus, it is beyond the scope of this study to address the implications of HOBr solubility on halogen processing in sea salt particles in any quantitative way. Qualitatively, however, it can be observed that if tropospheric particles are sufficiently acidic, the solubility of HOBr may be decreased slightly relative to that in pure water, as shown in Figure 2.

Two stratospheric cases of interest, current and future, are outlined in Table 1. For conditions representative of winter high latitudes or the tropical tropopause region, it is evident that the solution concentrations of HOBr, HBr, and HCl will be comparable in the current lower stratosphere (LS). In a future scenario, where chlorine loading and temperature decrease, but bromine and water vapor increase <Katja & Jim, any suggestions for references here would be greatly appreciated !>, solution concentrations of HBr and HCl increase in roughly equal amounts, but that of HOBr will stay significantly lower, due to the near independence of its solubility on acidity. To evaluate the interference of other pathways (Reactions 1 and 3) in the conversion of HCl to BrCl (Reaction 2), the second order rate constants, k_{II}, for each reaction need to be known. We were unable to extract a value for either k(HOBr + HBr) or k(HOBr + HCl) from the present work, and only k values for HOBr + HCl have been previously reported

(Hanson, 2003; Waschewsky and Abbatt, 1999). Abbatt (1995) does give a lower limit for k(HOBr + HBr) at one set of experimental conditions, which suggests that rate constant is similar to or slightly less than k(HOBr + HCl), so we presume that all three rate constants are approximately equal. The parameterization of Hanson (2003) for k(HOBr + HCl) as a function of temperature and wt% H_2SO_4 was used to calculate rate constants for the two stratospheric cases. Since Rate = k [HOBr] [HX] (where square brackets denote solution concentrations and X = Cl, Br, or BrO), we can calculate relative rates for the three channels based on the calculated solution concentrations and estimated values of k_{II}.

As shown in Table 1, the calculated rates suggest that reaction with HCl will account for ~85 - 90% of the solution phase reactivity of HOBr in the cases illustrated. Thus, reactions of HOBr with itself and HBr will reduce the possible activation of HCl to BrCl by only ~15%. Although all solution phase concentrations increase in the wetter, colder scenario, the rate coefficient, k_{II}, decreases more significantly, reducing the rate of BrCl production by a factor of roughly seven. It must be stressed, however, that these results are highly dependent on the presumed second order rate constants, and further measurements of those values would greatly improve the accuracy and relevance of these illustrative calculations.

Table 1

	Current Lower Stratosphere	Future Lower Stratosphere	References & Notes
T	210 K	205 K	100 mbar; 15-16 km
water (g)	4 ppm	5 ppm	
aerosol composition	66 wt% H_2SO_4	60 wt% H_2SO_4	Steele and Hamill, 1981
HOBr (g)	1 ppt	1.2 ppt	
HBr (g)	2 ppt	3 ppt	Johnson et al., 1995
HCl (g)	1.5 ppb	1 ppb	
H^* HOBr	8.6×10^5 M atm^{-1}	1.6×10^6 M atm^{-1}	this work
H^* HBr	3.2×10^5 M atm^{-1}	8.1×10^6 M atm^{-1}	Sander et al., 2003
H^* HCl	1×10^4 M atm^{-1}	1.3×10^5 M atm^{-1}	(Wexler and Clegg, 2002); second column estimated from lowest RH possible with AIM model (58 wt%), for first column H^* from AIM reduced by ratios seen by (Williams and Golden, 1993; Hanson & Ravishankara 1993) for H_2SO_4 increased by 8 wt%
[HOBr]	8.5×10^{-8} M	1.9×10^{-7} M	
[HBr]	6.2×10^{-8} M	2.4×10^{-6} M	
[HCl]	1.5×10^{-6} M	1.3×10^{-5} M	
k_{II} HOBr + HX	6.1×10^5 M^{-1} s^{-1}	4.0×10^3 M^{-1} s^{-1}	Hanson, 2003
Rate for HOBr + HOBr	4.4×10^{-9} M s^{-1}	1.5×10^{-10} M s^{-1}	
Rate for HOBr + HBr	3.2×10^{-9} M s^{-1}	1.9×10^{-9} M s^{-1}	

Rate for HOBr + HCl	7.6 x 10^8 M s^{-1}	1.0 x 10^{-8} M s^{-1}

Assuming an aerosol volume density of 1×10^{-13} cm^3 cm^{-3} and no diffusion limitations, current LS conditions would lead to ~4-5 molecule BrCl produced per cm^3 per second. Compared to the rate for Cl activation via HCl + OH (~2×10^3 molecule cm^{-3} s^{-1} if [OH] = 1×10^6 molecule cm^{-3} with the rate taken from *Sander et al.* (2003), the heterogeneous activation route can be seen to be minor under background aerosol conditions, as discussed by others (Hanson, 2003; Waschewsky and Abbatt, 1999). If aerosol volumes were increased 50- to 100-fold due to volcanic injection, however, enhanced Cl activation via heterogeneous chemistry would need to be considered.

Furthermore, it is instructive to consider the possible conditions of a colder, wetter stratosphere. Reduction in aerosol acidity leads to a strongly reduced rate constant, suppressing the role of this mechanism even further. However, this strong sensitivity points to the possible enhanced role of this process under conditions where sulfate aerosols are more concentrated than ~ 65 wt% H$_2$SO$_4$. Thus, a role for chlorine activation via HOBr heterogeneous chemistry may exist under strongly acidic (warm, dry) conditions, or under conditions of enhanced stratospheric aerosol loading. In contrast, it is unlikely that any significant perturbation of HOBr will occur, as the formation of HOBr via BrONO$_2$ hydrolysis is ~20 - 40 times faster (Lary et al., 1996) than loss via heterogeneous reaction.

5. Conclusions

The solubility of hypobromous acid has been measured in cold H$_2$SO$_4$/H$_2$O solutions representative of stratospheric sulfate aerosols. For the conditions studied here (45 - 70 wt% H$_2$SO$_4$, 201 - 252 K), the effective Henry's law coefficient, H^*, ranges from $10^4 – 10^7$ mol L^{-1} atm^{-1}, with little acidity dependence at temperatures warmer than ~ 213 K. The enthalpy of solution for HOBr dissolving in 55-70 wt% H$_2$SO$_4$ was found to be -46.2 kJ mol^{-1}, in good agreement with previous studies. In 45 wt% H$_2$SO$_4$, ΔH = -70.2 kJ mol^{-1}. HOBr solubility in these solutions was found to be similar to those expected in pure water, which may explain the lack of composition dependence. The relative independence of solubility on acidity implies that heterogeneous chemistry involving HOBr will be more important (relative to processes involving HBr and other strong acids) under conditions which favor more acidic particles, as the solubility of HOBr will not decrease significantly.

7. Appendix:

Each exposure of HOBr to liquid sulfuric acid solutions produces a time trace of mass spectrometer signals which are proportional to gas partial pressures. These signals are converted to time-varying uptake coefficient values, γ, via Eq. 4. Each set of γ values contains information about the solubility of HOBr and its irreversible reaction in solution. In this study, each data set was fit with the three-parameter nonlinear equation (Eq. 5) which approximates the coupled differential equations describing dissolution and reaction of a gas in a planar liquid (Danckwerts, 1970).

Estimates for the parameters (H^*, β, k) were found using a minimization program written for MATLAB by a team of students at San Jose State University (SJSU). Using nonlinear, multivariate methods, the parameter values were found by minimizing the sum of the squared errors (SSE) between the equation and the data. Since k is typically small, and is sometimes zero, it is reasonable to assume $k = 0$ and solve the reduced (linear) equation to generate a starting estimate for the other two parameters. The minimum SSE was found via a numerical search method similar to simulated annealing.

Because all three parameters must be non-negative, we cannot assume that these parameter estimates follow a Normal distribution, and thus the standard methods for computing confidence intervals cannot be used. Instead, bootstrap methods were used to determine 95% confidence limits for the unknown parameters.

Lastly, a protocol was developed to objectively identify suspicious or biased data sets. Three tests were applied to the residuals (the difference between each data point and the value

calculated from the best-fit parameters). The first identifies points beyond three standard deviations away from the mean of the residuals. The second test highlights any series of nine points on one side of the mean. Such a series may be a signal of unsteadiness in the laboratory process. The last test seeks two out of three consecutive points beyond two standard deviations on the same side of the mean. Each of these events has < 0.5% probability of occurring in a Normally distributed data set, thus experiments which displayed more events than expected (based on the number of points in each set) were discarded.

The parameter values determined with the SJSU MATLAB code were checked against values determined with a separate program written using the statistical software package S-PLUS and its function specifically designed for minimization of non-linear equations. The parameter estimates found using S-PLUS and those found by MATLAB differed by less than one percent. A number of the parameter sets were also compared to values found with the Kaleidagraph software package, and excellent agreement was also obtained.

The MATLAB program used in this work was developed under the supervision of Prof. Steven Crunk as part of the Center for Applied Mathematics and Computer Science (CAMCOS, Prof. Timothy Hsu, Director) student research program in the SJSU Department of Mathematics. Team members Greg Holsclaw, Eleanore Jehung, Sylvia Law, Chingchia Ly, Joe Metz, and Tracy Skovmand (all SJSU students) performed the work. Funding for the project was provided by the Henry Woodward Fund.

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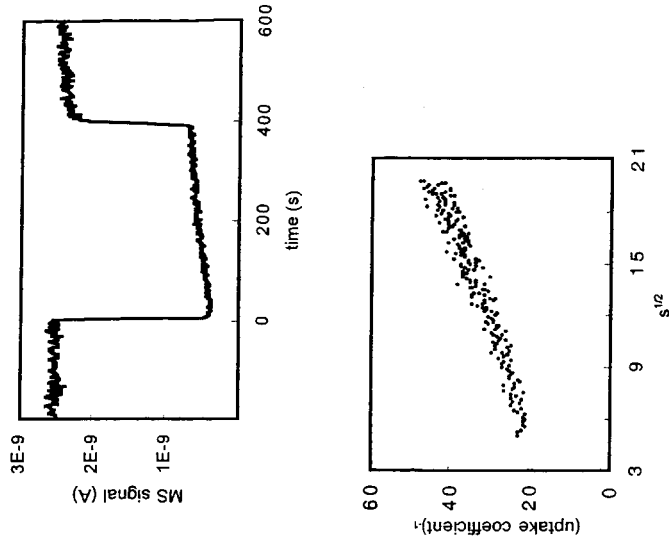
Figures:

Figure 1 (a): Mass spectrometer signal as a function of time showing behavior of HO⁸¹Br upon exposure to 45.3 wt% H₂SO₄ solution at 219.0 K. Exposure was begun at 0 s and ended at 400 s. Panel (b): Inverse of uptake coefficient as a function of (time)^(1/2) yielding $H* = 6.3 \times 10^5$ M atm⁻¹.

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Figure 3: Inverse of uptake coefficient as a function of $(time)^{1/2}$ for exposure of HOBr to 70.1 wt% H_2SO_4 at 211.9 K. The observed deviation from linearity indicates reactive uptake processes in addition to solubility.
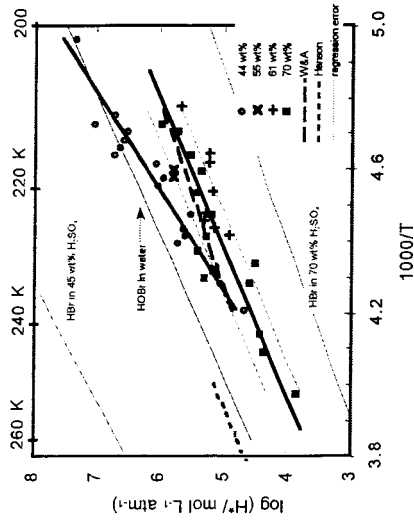
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Figure 2: Log of the effective Henry's law coefficient as a function of inverse temperature. Experimental results for HOBr solubility in 44 – 45 wt% H_2SO_4 are averaged in 1 K bins and plotted as green circles. The solid green line is the best fit to these data, $\log H^* = 3665/T - 10.63$. Other 1 K average results shown are: crosses (X) for 55 wt% H_2SO_4, plus signs (+) for 61 wt%, and squares for 70 wt%. All data for 55 – 70 wt% were then combined in 1 K intervals; the resulting linear fit is shown as the solid black line ($\log H^* = 2412/T - 5.55$). The thin grey lines show the best fit plus and minus one standard error of the regression, as explained in the text. For comparison, the results of *Waschewsky and Abbatt* (1999) are shown over their experimental temperature range as the dashed blue line, while the warmer temperature results of Hanson are given by the dotted red line at the left side of the figure. Thin brown lines at the top and bottom show the solubility of HBr, as calculated from *Sander et al.* (2003).
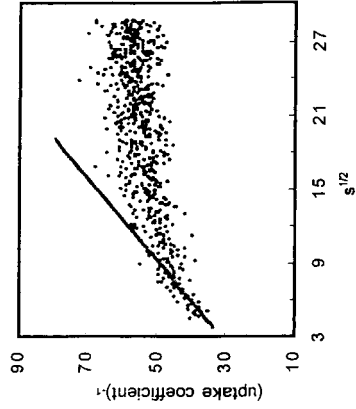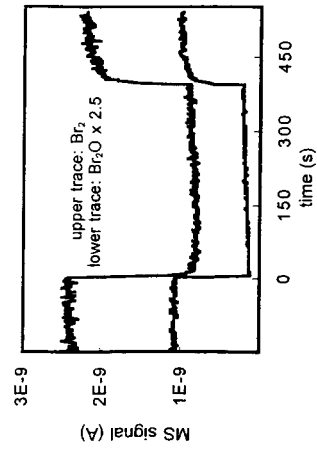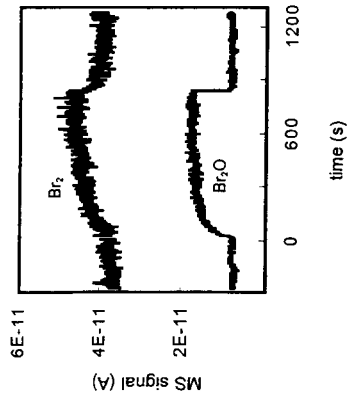
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Figure 4 (a): Mass spectrometer signals as a function of time showing behavior of Br_2 (m/z = 160) and Br_2O (176) upon exposure to 45.3 wt% H_2SO_4 solution at 219.0 K. Panel (b): MS signals for the same species during exposure to 70.1 wt% H_2SO_4 at 211.9 K

21

Uptake of Hypobromous Acid (HOBr) by Aqueous Sulfuric Acid Solutions:

Low -Temperature Solubility and Reaction

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Abstract:

Hypobromous acid (HOBr) is a key species linking inorganic bromine to the chlorine and odd hydrogen chemical families. We have measured the solubility of HOBr in 45 - 70 wt% sulfuric acid solutions representative of upper tropospheric and lower stratospheric aerosol composition. Over the temperature range 201 - 252 K, HOBr is quite soluble in sulfuric acid, with an effective Henry's law coefficient, $H* = 10^4 - 10^7$ mol L^{-1} atm^{-1}. $H*$ is inversely dependent on temperature, with $\Delta H = -46.2$ kJ mol^{-1} and $\Delta S = -106.2$ J mol^{-1} K^{-1} for 55 - 70 wt% H_2SO_4 solutions. Our study includes temperatures which overlap both previous measurements of HOBr solubility. For uptake into aqueous 45 wt% H_2SO_4, the solubility can be described by log $H* = 3665/T - 10.63$. For 55 – 70 wt% H_2SO_4, log $H* = 2412/T - 5.55$. At temperatures colder than ~ 213 K, the solubility of HOBr in 45 wt% H_2SO_4 is noticeably larger than in 70 wt% H_2SO_4. The solubility of HOBr is comparable to that of HBr, indicating that upper tropospheric and lower stratospheric aerosols should contain equilibrium concentrations of HOBr which equal or exceed those of HBr. Our measurements indicate chemical reaction of HOBr upon uptake into aqueous sulfuric acid in the presence of other brominated gases followed by evolution of gaseous products including Br_2O and Br_2, particularly at 70 wt% H_2SO_4.

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