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Heterogeneous Interactions of HBr and HOCl with Cold Sulfuric Acid Solutions: Implications for Arctic Boundary Layer Bromine Chemistry

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The heterogeneous interactions of HBr and HOCl with cold sulfuric acid solutions have been measured with a low-temperature, coated-wall flow tube coupled to an electron-impact mass spectrometer. In particular, (i) the effective Henry's law constants (H^*) for the solubility of HBr in sulfuric acid solutions (40.3−60.5 wt %) have been determined by measuring the HBr partial pressure as a function of temperature, (ii) the values of $HD^{1/2}$ of HOCl, where D is the liquid-phase diffusion coefficient, have been measured by monitoring the time-dependent uptake of HOCl over sulfuric acid solutions (59.7−69.3 wt %), and (iii) when the steady-state decay of gas-phase HOCl is monitored in the presence of an excess of HBr, the liquid-phase rate constant for reaction between dissolved HOCl and HBr has been measured to be 2×10^6 M^{-1} s^{-1} in 69.3 wt % acid at 228 K. When coupled with field observations from the Arctic boundary layer, these experimental results suggest that (i) heterogeneous interactions involving HOCl could be important in maintaining ozone loss rates by acting as an efficient activation mechanism for HBr in the springtime and (ii) as a result of the extremely large Henry's law constants for HBr in dilute sulfuric acid, sulfate particles in the boundary layer may contain significant amounts of dissolved HBr.

Introduction

There is now considerable interest in the role that photochemically active halogen species play as oxidants in the Earth's boundary layer. Although it is generally recognized that the hydroxyl radical is the dominant oxidizing radical in the free troposphere, the release of chlorine and bromine from sea-salt aerosols and the potential contribution of halogens from biological sources can lead to the presence of significant levels of photochemically active halogens in the planetary boundary layer. For example, in the Arctic boundary layer in springtime extremely high levels of bromine free radicals are associated with low levels of ground-level ozone.[1] Simultaneously, by observing that hydrocarbon oxidation rates in the field correlate closely with known hydrocarbon/Cl atom reactivities, it has been indirectly observed that high levels of photochemically active chlorine are present in the Arctic simultaneous with the high levels of bromine.[2] Whether high levels of the two halogens are set independently by similar chemical processes or whether elevated levels of one drive high levels of the other is not yet known. As a second example, high levels of photochemically active chlorine have been observed away from the poles by Pszenny et al.[3] Over the ocean at midlatitudes, these workers have inferred that a few hundred parts per trillion of active chlorine, probably in the form of either Cl_2 or HOCl, can be present.

A central issue required to understand the chemistry of these regions is the manner by which the halogens are maintained in their active forms. In the case of the Arctic troposphere, the time scale for formation of HBr is extremely rapid, much faster than any gas-phase HBr activation mechanism. Thus, it is very likely that there is a heterogeneous mechanism operating that maintains Br in an active form during one of these ozone depletion events.[4−7] Although Fan and Jacob have suggested that the heterogeneous reaction between HOBr and HBr could serve such a role,[7] it is possible that a number of other reactions are also important. In particular, high levels of active chlorine could activate HBr via reaction with species such as HOCl and Cl_2:

$$\mathrm{HOCl + HBr \rightarrow BrCl + H_2O} \tag{1}$$

$$\mathrm{Cl_2 + HBr \rightarrow BrCl + HCl} \tag{2}$$

To make an initial assessment of the rate of reaction 1 in the atmosphere, we have performed a number of studies of the heterogeneous chemistry of HBr and HOCl in sulfuric acid solutions. In particular, for a variety of sulfuric acid solutions, we report measurements of the solubilities of HBr and of the quantity $HD^{1/2}$ (H is Henry's law constant and D the liquid-phase diffusion constant) for the uptake of HOCl. Also, we have measured the liquid-phase rate constant for reaction 1 for a 69.3 wt % solution at 228 K. Together, these results are used to make a preliminary assessment of whether reaction 1 is likely to be important as a mechanism to activate HBr in the Arctic boundary layer springtime. The measurements of the solubility of HBr are also used to assess to what extent HBr will be partitioned from the gas phase to sulfuric acid aerosol in the boundary layer.

Since they pertain to atmospheric chemistry, there are now a number of published laboratory studies of the heterogeneous interactions between the species HOX and HY, where X and Y are both halogens.[8−15] Briefly, it is well recognized that reactions 3−5 proceed readily on ice surfaces:[8,12,13,15]

$$\mathrm{HOCl + HCl \rightarrow Cl_2 + H_2O} \tag{3}$$

$$\mathrm{HOBr + HBr \rightarrow Br_2 + H_2O} \tag{4}$$

$$\mathrm{HOBr + HCl \rightarrow BrCl + H_2O} \tag{5}$$

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Reaction 3 has been extensively studied in sulfuric acid solutions,[9,10] whereas considerably less work has been performed on the liquid-phase reactions 4 and 5.[11,14] To our knowledge, the work reported here is the first on reaction 1.

Experimental Section

For the most part, experiments were performed in a low-temperature, low-pressure, coated-wall flow tube of a design similar to that described in ref 14. A differentially pumped, electron-impact mass spectrometer is coupled to the flow tube to monitor the composition of the gas phase. Detection limits ($S/N = 1$, 2 s integration) were on the order of 3×10^9 molecules/cm^3 for HOCl and somewhat higher for HBr, dependent upon the partial pressure of H_2O in the flow tube (see below).

1. Vapor Pressure of HBr over Sulfuric Acid Solutions. Gas-phase HBr partial pressures were monitored for a variety of solutions of HBr in sulfuric acid. In particular, 0.10−0.30 M solutions of HBr in sulfuric acid were prepared by mixing appropriate volumes of aqueous stock solutions of HBr (48 wt %) and H_2SO_4 (96 wt %). The sulfuric acid molarities of the solutions were determined by titration with NaOH solutions, taking into account the acidity in the solution due to the presence of HBr. To convert the molarity into a weight percentage of sulfuric acid, the density of the solutions was determined by weighing a known volume of the solution. For example, the measured density of the 0.3 M HBr, 48.8 wt % sulfuric acid solution at room temperature was 1.40 g/mL, somewhat higher than the literature value of 1.39 g/mL for 48.8 wt % sulfuric acid. Overall, when the uncertainties in the titrations are taken into consideration, the sulfuric acid compositions are believed to be accurate to the ±0.2 wt % level.

To perform the vapor pressure measurement, 15 mL of the solution was placed into a 2.6 cm o.d., 33 cm long Pyrex tube that had each end half-capped and that sat snugly in the cold flow tube. The solution was allowed to reach thermal equilibrium with the flow tube before a small flow of carrier gas was established through the tube at a total pressure of roughly 2 Torr. The carrier gas consisted of both He (∼60 sccm) and H_2O from a bubbler in proportions that set the partial pressure of water within 20% of the vapor pressure of water over the cold sulfuric acid solution.[16] The HBr mass spectrometer signal, monitored at its parent ion, was recorded until it was steady. To test that the carrier gas was saturated with the HBr from the sulfuric acid solution, the effective Henry's law constant measured on a 60.5 wt % solution at 258 K was found to be independent of the carrier gas flow when the helium flow was varied by a factor of 5 at the same total pressure. This implies that the rate of HBr mass flow, via either diffusion of HBr through the sulfuric acid film or through the He carrier gas, does not determine the partial pressure of HBr measured at the downstream end of the flow tube. Solutions were regularly titrated after a vapor pressure measurement that indicated that their compositions did not change as a result of the experiment. Similarly, given the HBr vapor pressures, the concentration of the HBr in the solution, and the total He flow rates, it is easily calculated that the HBr content of the solutions did not change significantly during a run.

For each set of measurements over a single solution, the sensitivity of the mass spectrometer to HBr was determined under the same flow conditions as were present during an HBr vapor pressure measurement. In particular, the solution was removed from the flow tube and the HBr signal was monitored when HBr was added to the flow tube in known amounts from a Pyrex reservoir filled with a dilute solution of HBr in He. In a flow tube without water vapor present, the detection limits for HBr were on the order of 5×10^9 molecules/cm^3. However, with high partial pressures of water, as were present in the studies of the 40.3 wt % solution, the HBr background signal arising from HBr adsorbed on the wall was substantial. That is, after the flow tube was exposed to HBr and then after the HBr flow was shut off, the background signal decreased only very slowly. As a result, the HBr detection limit for the experiments with the 40.3 wt % solution was roughly an order of magnitude higher, 5×10^{10} molecules/cm^3, than for the other experiments.

An additional set of HBr vapor pressure measurements was performed over HBr/sulfuric acid solutions at room temperature. As configured, it was inconvenient to use the mass spectrometer for solutions with such high vapor pressures of H_2O, so instead, we elected to use a different technique where we passed a flow of dry N_2 through a bubbler containing an H_2SO_4/HBr solution of known composition held at 298 K. This N_2 flow then passed through a second bubbler containing deionized water that acted as a trap for HBr in the flow. By measuring the electrical conductivity of the solution in the second bubbler after a period of time during which we trapped HBr, we could readily calculate the number of moles of HBr in the trap and, thus, the vapor pressure of HBr in the HBr/H_2SO_4 solution. Total flows of N_2 were approximately 600 sccm, and concentrations of HBr in the sulfuric acid solutions were 0.34−0.50 M.

A number of experiments were performed to validate this technique of measuring vapor pressures. First, to test the assumption that the flow leaving the first trap was saturated with HBr, we varied the total flow of N_2. In particular, by reducing the N_2 flow by a factor of 2 from the normal operating conditions of 600 sccm, we measured within the precision of the experiment, the same HBr partial pressure over a 67.6 wt % sulfuric acid solution. Second, to test that the flow line connecting the two traps is conditioned to the flow of HBr, we would always operate with a minimum conditioning time of 15 min before we would direct the flow into the second bubbler and start the HBr collection process. Lengthening this collection time by a factor of 3 had no effect on the results. Last, to test that we were detecting electrical conductivity arising from HBr and not from some other species emanating from the sulfuric acid solution (e.g., H_2SO_4 vapor), we ran control experiments on pure sulfuric acid solutions, i.e., solutions that contained no HBr. Initially, these control runs did give rise to an appreciable signal (150 μmho/cm) most likely due to a small number of sulfuric acid particles leaving the first bubbler. However, we were able to entirely remove this signal by placing a glass-fiber filter along the line connecting the two traps. All the experimental results given below were performed with this glass-fiber filter in place. Effective Henry's law constants were also independent of the collection times, which varied from 8−30 min. Electrical conductivities ranged from 35 to 17 000 μmho/cm, being highly dependent upon the solution being studied. The background conductivity of the distilled/deionized water in our lab is 0.6 μmho/cm.

2. HOCl Time-Dependent Uptake by Sulfuric Acid Solutions. HOCl time-dependent uptake studies were performed in a manner equivalent to that described in detail in a previous work.[14] Briefly, the inner walls of a 2.5 cm i.d. Pyrex tube were coated with sulfuric acid solution, and the tube was then inserted into the cold flow tube and allowed to thermally equilibrate. The sulfuric acid solution coated the walls of the tube throughout the run with a film many 10's of micrometers thick. A steady-state flow of HOCl was established through a movable, axial injector positioned with its tip downstream of the end of the sulfuric acid film. When the HOCl mass spectrometer signal was steady, the injector was quickly withdrawn on the time scale of a second or so to an upstream position so that HOCl was now being exposed to and being taken up by the solution. At a later time, the injector was pushed back to its original position and the HOCl was seen to desorb (see Results and Discussion section). These experiments were performed at a total pressure of roughly 1 Torr of He. The majority of the carrier gas entered at the back of the flow tube, whereas roughly 10% entered through the movable injector as a carrier gas for the HOCl. The HOCl source was a bubbler held at 273 K that contained an aqueous HOCl solution prepared from the reaction between $MgSO_4$ and NaOCl.[12,17] When a small fraction of the main He carrier gas was passed through a water bubbler, water vapor was added to the flow tube at partial pressures within 10% of the vapor pressure of water over the sulfuric acid film.

An upper limit to the partial pressures of HOCl used in this work was determined by passing the flow from the HOCl bubbler through a 50 cm long absorption cell held at atmospheric pressure. The absorption at 254 nm was monitored for typical operating conditions for the HOCl experiments. By assuming that HOCl was the sole absorber at this wavelength, it was determined that HOCl concentrations were no more than $(1-2) \times 10^{11}$ molecules/cm^3 for these experiments.

3. HOCl/HBr Kinetics in 69.3 wt % Sulfuric Acid Solution. The liquid-phase reaction kinetics between HOCl and HBr were studied in a 69.3 wt % sulfuric acid solution at 228 K by simultaneously admitting HOCl and HBr to the flow tube with HBr in excess concentration. Specifically, both HOCl and HBr were added via the axial injector. However, to avoid a reaction between the two prior to entering the flow tube, they were physically isolated in the injector by adding the HBr through a 1.6 mm o.d. Teflon tube that ran inside the length of the axial injector. The sulfuric acid solution coated the wall as described above for the HOCl uptake experiments. To measure an uptake coefficient, first-order decays of HOCl were measured at steady-state as a function of the position of the injector in the flow tube. Initial concentrations of HOCl in the flow tube were between 5×10^{10} and 2×10^{11} molecules/cm^3.

To show that HBr has sufficiently saturated the upper portion of the sulfuric acid film, we can calculate the degree of saturation at the reactodiffusive depth $l_{RD} = (D_l/k^I)^{1/2}$, where D_l is the liquid-phase diffusion coefficient ($\sim 10^{-7}$ cm^2/s) and k^I is the liquid-phase first-order rate constant (see Results and Disscusion section)) for this reaction. Specifically, following the approach of Dankwerts,[18] it can be shown that at a typical reactodiffusive depth, 0.15 μm, the HBr concentration is 99% of the surface value after the film has been exposed to HBr for 5 s, i.e., the minimum time before a measurement is taken.

Results and Discussion

1. Vapor Pressure of HBr over Cold Sulfuric Acid Solutions. Results from the HBr vapor pressure experiments are given in Figure 1 and Tables 1 and 2, where values are given for the effective Henry's law constant, H^*, which is defined as $H^* = [HBr]_{soln}/P_{HBr}$. Table 3 gives the coefficients for a least-squares fit to the data in Figure 1, along with the calculated enthalpies and entropies of HBr solvation. Also included in Figure 1 are determinations of HBr Henry's law constants from an earlier study,[14] which were made by measuring the value of $H^*D^{1/2}$ and by calculating the value of the liquid-phase diffusion coefficient according to the procedure outlined by Williams and Long.[19] In particular, this calculation scales a room temperature value for the diffusion coefficient of HBr in water by the viscosity and temperature of the sulfuric acid solutions. From the results for the solutions of close to 60 wt % sulfuric acid composition, it is seen that the two techniques appear to give results that are in very good agreement with each other. Also included in the figure as dashed lines are the only other measurements of the effective HBr Henry's law constant in sulfuric acid, those of Williams et al.[20] The two sets of results appear to be highly consistent with each other, as is shown most clearly for the solutions that have compositions close to 60 wt % acid.

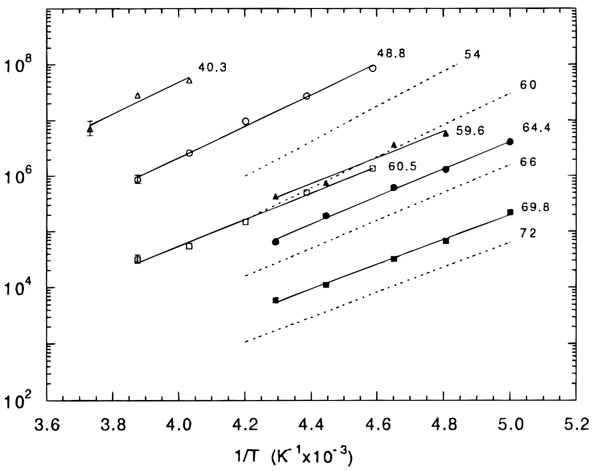

Figure 1. H^* for HBr as a function of temperature and sulfuric acid composition (labels in figure as wt %). Symbols and solid lines are results from this work and from ref 14. Dotted lines are results from Williams et al.[20] Representative error estimates are shown at one point for each set of measurements.

TABLE 1: H^* as a Function of Temperature and the Sulfuric Acid Composition As Determined from the Mass Spectrometry Vapor Pressure Measurements

H_2SO_4 (wt %)	T (K)	H^* (M/atm)
40.3	248	5.2×10^7
40.3	258	2.8×10^7
40.3	268	7.1×10^6
48.8	218	8.5×10^7
48.8	228	2.7×10^7
48.8	238	9.6×10^6
48.8	248	2.6×10^6
48.8	258	8.6×10^5
60.5	218	1.4×10^6
60.5	228	5.1×10^5
60.5	238	1.5×10^5
60.5	248	5.5×10^4
60.5	258	3.2×10^4

TABLE 2: H^* for HBr as a Function of the Sulfuric Acid Composition As Determined from the Electrical Conductivity Vapor Pressure Measurements

H_2SO_4 (wt %)	T (K)	H^* (M/atm)
49.5	298	5.5×10^4
57.3	298	3.9×10^3
64.4	298	3.8×10^2
67.6	298	1.2×10^2

When compared to estimates based on thermodynamic calculations of H^*(HBr) made by Carslaw et al.,[21] there is reasonable agreement with our measurements for the most concentrated solutions but very poor agreement for the more dilute solutions. For example, taking a temperature of 238 K for comparison, Carslaw et al. calculate effective Henry's law constants that are roughly factors of 1.5, 5, 20, and 15 times larger than those measured in our laboratory for solutions close to 70, 60, 50, and 40 wt % sulfuric acid, respectively. This discrepancy has been noted previously by Carslaw et al. when

TABLE 3: Coefficients from Least-Squares Fit of log(H^*(HBr)) = $A/T + B$ (with 1 − σ Uncertainties), along with Calculated Enthalpy and Entropy of Solvation[a,b,c]

H_2SO_4 (wt %)	A	B	ΔH_{sol} (kcal mol^{-1})	ΔS_{sol} (cal mol^{-1} K^{-1})
40.3	$(2.9 \pm 0.7) \times 10^3$	-3.8 ± 2.7	-13.1 ± 3.2	-20 ± 12
48.8	$(2.8 \pm 0.1) \times 10^3$	-4.9 ± 0.5	-12.9 ± 0.5	-26 ± 2
59.6	$(2.4 \pm 0.3) \times 10^3$	-4.5 ± 1.3	-10.8 ± 1.3	-25 ± 6
60.5	$(2.4 \pm 0.1) \times 10^3$	-4.9 ± 0.5	-11.0 ± 0.6	-27 ± 3
64.4	$(2.5 \pm 0.1) \times 10^3$	-5.8 ± 0.4	-11.4 ± 0.4	-31 ± 2
69.8	$(2.2 \pm 0.1) \times 10^3$	-5.8 ± 0.4	-10.1 ± 0.4	-31 ± 2

[a] H^*(HBr) in M/atm, T in Kelvin. [b] Data are also included from ref 14. [c] ΔS_{sol} calculated as in ref 20.

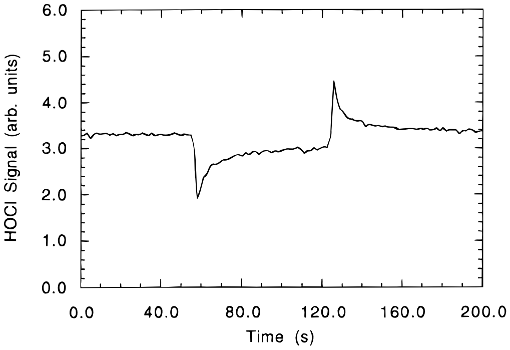

Figure 2. HOCl signal for uptake and desorption on a 69.3 wt % sulfuric acid surface at 208 K.

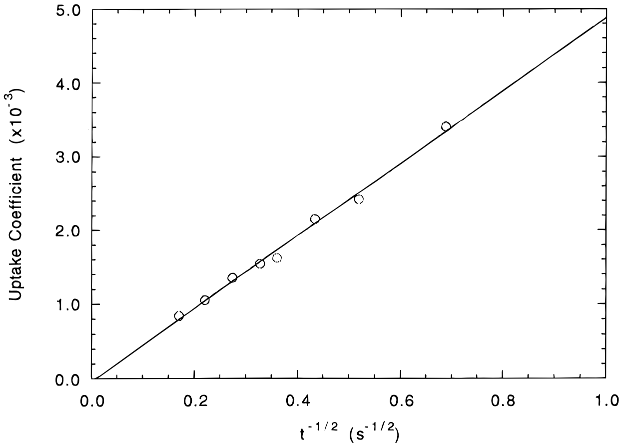

Figure 3. Uptake coefficient for HOCl as a function of $t^{-1/2}$ for the data shown in Figure 2.

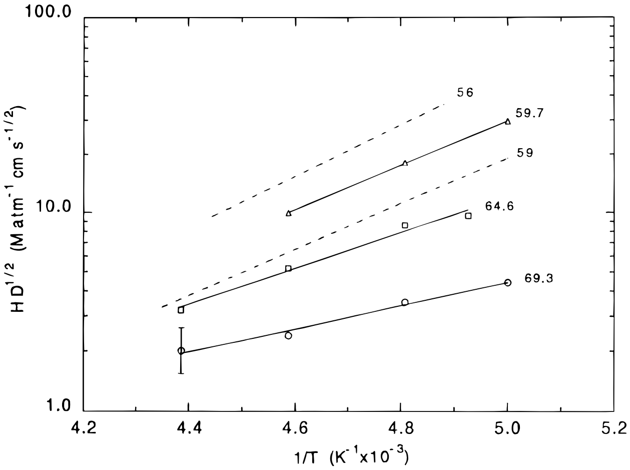

Figure 4. $HD^{1/2}$ for HOCl as a function of temperature and sulfuric acid composition (labels in figure as wt %). Symbols and solid lines are results from this work. Dashed lines are results from Hanson and Ravishankara.[9] A representative error estimate is shown for one point.

they compared their calculations to the experimental results of Williams et al.[20] Since the disagreement is similar to our data set, it appears as though the thermodynamic parametrization is reasonably accurate for concentrated sulfuric acid solutions (~70 wt %) but not for more dilute solutions.

There are no measurements or calculated values to which we can compare the room temperature measurements of the effective Henry's law constants. However, the data at room temperature appear to be reasonably consistent with extrapolations of the cold temperature data to warmer temperatures. For example, the room temperature Henry's law constant on the 64.4 wt % solution was measured to be 3.8 × 10^2 M/atm. If we extrapolate in a log−linear manner the values of H^* reported in ref 14 for a 64.4 wt % solution to 298 K, the value we obtain is 3.4 × 10^2 M/atm. A similar comparison for the solutions close to 50 wt % composition yields reasonable agreement at 298 K: $H^* = 5.5 \times 10^4$ M/atm for 49.5 wt % solutions by the electrical conductivity technique and 3.3 × 10^4 for 48.8 wt % solutions by the mass spectrometry technique.

In general, we estimate errors in the effective Henry's law constants measured by mass spectrometry to be on the order of ±25% for the measurements over the 48.8 and 60.5 wt % solutions and ±40% for the measurements over the 40.3 wt % solution. From the scatter in the data, we estimate somewhat higher uncertainties, on the order of a factor of 2, in the effective Henry's law constants measured by the electrical conductivity technique.

2. HOCl Time-Dependent Uptake by Sulfuric Acid Solutions. A typical uptake/desorption measurement of HOCl on sulfuric acid is shown in Figure 2 for a 69.3 wt % solution at 208 K. The injector is withdrawn from an initial upstream position at a time of 55 s and then pushed back in to its original position at 122 s. Data in Figure 2 are analyzed according to eq 6 in order to determine the value of $HD^{1/2}$:

$$\gamma^{\mathrm{HOCl}}(t) = \frac{4RTH\sqrt{D}}{c\sqrt{\pi t}} \qquad (6)$$

where $\gamma(t)$ is the time-dependent uptake coefficient calculated from the decay of the HOCl signal between its original steady-state value and its time-dependent value. R is the ideal gas constant, and c is the mean molecular speed. To account for the effects of non-plug−flow conditions that arise from wall loss, the standard procedure due to Brown was used with the value for the HOCl-in-He diffusion coefficient taken from ref 12.[22] Figure 3 demonstrates that the time-dependent uptake coefficient is a linear function of $t^{-1/2}$ for times longer than roughly 2 s or so. For the data presented in Figure 2, the value of $HD^{1/2}$ is calculated to be 3.5 (M/atm)(cm^2/s)$^{1/2}$.

As illustrated in Figure 4 and Table 4, similar experiments were performed over a range of sulfuric acid solutions and temperatures. In particular, the specific goal of these experiments was to determine the value of $HD^{1/2}$ on solutions close to 70 wt % to aid in the measurement of the liquid-phase rate constant between HOCl and HBr in that solution. Each value reported in Figure 4 and Table 4 is the average of roughly three measurements. In the figure, comparison is made to the only

TABLE 4: $HD^{1/2}$ for HOCl as a Function of Temperature and the Sulfuric Acid Composition

H_2SO_4 (wt %)	T (K)	$HD^{1/2}$ (M atm^{-1} cm s$^{-1/2}$)
59.7	200	29
59.7	208	18
59.7	218	9.9
64.6	203	9.6
64.6	208	8.6
64.6	218	5.2
64.6	228	3.2
69.3	200	4.4
69.3	208	3.5
69.3	218	2.4
69.3	228	2.0

other experimental measurements of this quantity in the literature, those of Hanson and Ravishankara.[9] There appears to be a small but significant, systematic disagreement for the solutions close to 60 wt % between these two sets of measurements, with our measurements roughly a factor of 1.5−2 times larger than those of Hanson and Ravishankara (we estimate errors in our measurements of ±25%). However, the dependence of the value of $HD^{1/2}$ on temperature is very similar. The cause of this discrepancy is unclear because previous measurements of the values of $HD^{1/2}$ for HCl in sulfuric acid from the two groups are in somewhat better agreement.[9,14]

Of potential concern in this work is whether the water vapor that arises from the HOCl source has any effect upon the measured values of $HD^{1/2}$. Consequently, we performed experiments on the 69.3 wt % sulfuric acid solution at 208 K where we trapped out the water vapor from the HOCl line prior to the point where HOCl is added to the flow tube. We chose to study this solution because it has the lowest water vapor pressure and would thus be the most susceptible to the influence of water vapor entering via the injector. Specifically, we added a cold trap held at 243 K between the HOCl bubbler and the needle value controlling the flow into the flow tube and performed the uptake experiment in the usual manner. It was observed by mass spectrometry that the cold trap did not affect the HOCl signal but that it reduced the amount of water entering with the HOCl by a factor of 13, close to the ratio of the vapor pressure of water in the HOCl bubbler held at 273 K and the vapor pressure of water over ice at 243 K. With this configuration, the partial pressure of water vapor arising in the flow tube from the addition of HOCl was about a factor of 2 smaller than the water vapor pressure over the sulfuric acid film itself. Measurements of $HD^{1/2}$ performed in this mode agreed with those performed without the cold trap to 5%. This indicates that the water vapor entering the flow tube via the injector does not affect the measured values of $HD^{1/2}$.

3. HOCl/HBr Kinetics in 69.3 wt % Sulfuric Acid Solution. A set of experiments was performed to determine the second-order, liquid-phase rate constant between HOCl and HBr in 69.3 wt % sulfuric acid solution at 228 K. This set of conditions was chosen because we have previously studied the liquid-phase chemistry of HOBr with both HBr and HCl under equivalent conditions (i.e., 69.8 wt % acid at 228 K),[14] making comparison between the two sets of data easier. In particular, eq 7 was used to determine the value of the liquid-phase rate constant from a set of measurements of the HOCl first-order decay under excess HBr:

$$\gamma^{\mathrm{HOCl}} = \frac{4RTH\sqrt{Dk^{\mathrm{II}}[\mathrm{HBr}]_{\mathrm{soln}}}}{c} \qquad (7)$$

where k^{II} is the liquid-phase rate constant and the concentration of HBr in the solution, $[\mathrm{HBr}]_{\mathrm{soln}}$, is determined from the partial pressure of HBr in the flow tube and the effective Henry's law constant for HBr. As with the time-dependent HOCl studies, the first-order decays were corrected for gas-phase diffusion effects.

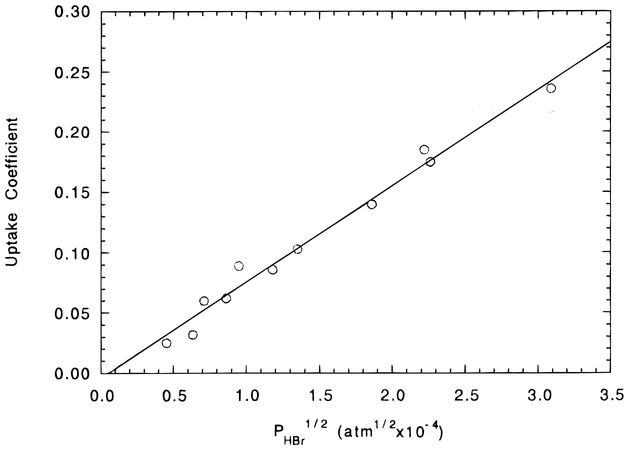

Figure 5. Uptake coefficient for HOCl as a function of partial pressure of HBr in the flow tube for a 69.3 wt % sulfuric acid film at 228 K.

In Figure 5, the uptake coefficient is plotted as a function of the partial pressure of HBr in the flow tube. By use of appropriate values for the effective Henry's law constant of HBr and for $HD^{1/2}$ of HOCl taken from Figures 1 and 4, respectively, the second-order rate constant is calculated from the data in Figure 5 to be 2 × 10^6 M^{-1} s^{-1}. As with all liquid-phase rate constants determined in this manner, there are relatively large uncertainties on the order of +100/−50% associated with this value.

For solutions of this viscosity a diffusion-limited rate constant for this reaction is on the order of a 10^7−10^8 M^{-1} s^{-1},[23] which implies that although this rate constant is large, the reaction kinetics are not fully under diffusion control. From other measurements of the rate constants of HOX/HY reactions (where X and Y are halogens) in cold, concentrated sulfuric acid solutions, it is now clear that all the reactions studied to date proceed with rate constants within a couple of orders of magnitude of the diffusion limit. In particular, for HOBr/HBr $k^{\mathrm{II}} > 5 \times 10^4$ M^{-1} s^{-1} in 69.8 wt % at 228 K,[14] for HOBr/HCl $k^{\mathrm{II}} = 1.4 \times 10^5$ M^{-1} s^{-1} in 69.8 wt % at 228 K and (0.3−1) × 10^5 M^{-1} s^{-1} in 60 wt % at 210 K,[11,14] and for HOCl/HCl, $k^{\mathrm{II}} = 1.6 \times 10^5$ M^{-1}s^{-1} in 60 wt % at 200−220 K[9] and 1.4 × 10^6 M^{-1} s^{-1} at 251 K.[10] By contrast, a room temperature measurement of the direct reaction between HOCl and Br^- in low-acidity aqueous solutions has yielded a somewhat smaller rate constant of 1.55 × 10^3 M^{-1} s^{-1}.[24]

Atmospheric Implications

With the data set presented here, and with other laboratory data and results from selected field measurements, we can make preliminary estimates of the efficiency at which HBr will be activated by HOCl and HOBr and determine the extent to which HBr will be partitioned into sulfuric acid aerosol in the Arctic boundary layer.

1. HBr Activation. Unlike the stratosphere where routes for formation of HBr are slow, HBr can much more readily form in the tropospheric boundary layer via reaction with high concentrations of HO_2 and via reactions with organic species. Consequently, when modeling ozone depletion episodes, photochemical models require heterogeneous reactions involving brominated species in order to maintain sufficiently high concentrations of bromine free radicals in order to destroy ozone at observed rates.[4,5,7] To estimate the rate of HBr activation via reactions 1 and 4, we will calculate uptake coefficients for HOCl and HOBr loss on sulfate particles by using the best available values for reactant liquid-phase solubilities, diffusivities, and kinetics, and by taking into account the dependence of the overall uptake coefficient on the size of the aerosol particles.[25]

To make these estimates, we need to make a number of assumptions concerning the nature of tropospheric aerosol particles. There is considerable evidence from field measurements that Arctic aerosol particles are highly acidic, being comprised, as Barrie has concluded,[26] of a combination of sulfuric acid formed by in situ oxidation of SO_2 and of ammonium bisulfate particles that have been transported from Eurasia. For the calculation here, we will assume that the aerosol particles are composed of sulfuric acid solutions that are in equilibrium with the ambient relative humidity. As illustrated by an average relative humidity value of 84 ± 14% reported by Staebler et al. from the recent Polar Sunrise Experiment,[27] the relative humidity is very high in a region with such a high degree of surface ice coverage. From the values of the vapor pressure of water over sulfuric acid solutions, this value implies a dilute sulfuric acid aerosol of 36 wt % composition.[16,28] Clearly, the relative humidity is a highly variable quantity in the atmosphere, and the composition of dilute sulfuric acid solutions is particularly dependent upon its value. Thus, for the sake of this model calculation, we will be conservative and assume that the aerosol particles have a composition of 40 wt % sulfuric acid.

For this composition of tropospheric sulfuric acid aerosol, an uptake coefficient for the HOCl reaction with dissolved HBr is calculated to be unity by using the following parameters: a temperature of 233 K, aerosol particle radius of 0.15 μm,[27] $HD^{1/2}$ for HOCl of 25 (M/atm)(cm^2/s)$^{1/2}$,[9] H^*(HBr) of 3×10^8 M/atm (this work), HBr partial pressure of 10^{-11} atm,[5,7] mass accommodation coefficient for HOCl of unity, and a liquid-phase rate constant of 2×10^6 M^{-1} s^{-1} (this work). Even though the liquid-phase rate constant is the most uncertain parameter in this calculation, since we are using a value measured on 69.3 wt % acid solutions whereas the aerosol particles present in the troposphere are expected to be more dilute, it can be noted that the uptake coefficient is still calculated to be large if the rate constant measured in low-acidity solutions at room temperature is used.[24]

When the equivalent calculation for the reaction between HOBr and HBr is made, an uptake coefficient of greater than 0.06 is calculated if the following parameters are used in addition to those specified above: $HD^{1/2}$ for HOBr of greater than 20 (M/atm)(cm^2/s)$^{1/2}$,[14] mass accommodation coefficient for HOBr of unity, and a liquid-phase rate constant of greater than 5×10^4 M^{-1} s^{-1}.[14] This calculated value for the uptake coefficient is very likely to be a lower limit to the true uptake coefficient for two reasons. One, the lower limit of $HD^{1/2}$(HOBr) being used is a value that was measured on a 70 wt % sulfuric acid solution at 228 K. The value of HOBr on a 40 wt % solution is expected to be orders of magnitude larger if the solubility of HOBr in sulfuric acid solutions behaves in a manner similar to that of HOCl, i.e., if the solubility of HOBr increases significantly as the concentration of the sulfuric acid decreases. Two, the value for the HOBr/HBr rate constant is a measured lower limit, and its value may very well be close to the diffusion limit for reasons described in ref 14.

From a photochemical modeling study of the springtime Arctic boundary layer, Fan and Jacob proposed that if the reaction between HOBr and HBr on sulfate aerosol occurred with a reaction probability for HOBr of 0.01, then HBr would be activated sufficiently rapidly to maintain ozone loss rates inferred from field data.[7] It is clear that HOBr may indeed be a significant activator of HBr, given the lower limit of 0.06 calculated for the HOBr uptake coefficient of reaction 4. Indeed, it is likely that the appropriate uptake coefficient may be close to unity. However, what has not previously been considered is the potential role that HOCl may also play as an activator of HBr. As mentioned in the Introduction, it has been indirectly observed in the Arctic that elevated levels of active chlorine are present.[2] If HOCl is present as one of the forms of this active chlorine at levels comparable to the 100's of pptv measured by Pszenny et al. at midlatitudes over the ocean,[3] then reaction 1 may be the dominant heterogeneous process activating HBr, considering that it is highly unlikely that HOBr amounts will exceed 10 pptv.

2. Partitioning of HBr to Tropospheric Sulfuric Acid Aerosol Particles. With the effective Henry's law constants measured in this work we can calculate the extent to which HBr will be partitioned to the aerosol condensed phase during the Arctic springtime. For 40 wt % sulfuric acid aerosol particles, the appropriate effective Henry's law constant is 3×10^8 M/atm at 233 K. By use of sulfate particle volume densities of 3×10^{-12} cm^3/cm^3,[1] it is calculated that approximately 2% of the gas-phase HBr will be in the aerosol condensed phase. This calculation, however, is strongly dependent upon the assumed value for the relative humidity. If instead we assume a higher relative humidity of ~90%, then the sulfate aerosol particles are expected to be considerably more dilute, somewhere between 30 and 35 wt %. From Figure 1 we can estimate that the appropriate effective Henry's law constant for such solutions at 233 K will be at least an order of magnitude larger than for 40 wt % aerosol. If this is the case, then the partitioning of HBr to the aerosol condensed phase will be correspondingly higher, on the order of 10's of percent.

Analysis of field measurements performed during the Polar Sunrise Experiment has led to the conclusion that the fraction of particulate bromide to gas-phase inorganic bromine in the Arctic springtime can range widely, from a few percent up to over 50%.[29] If HBr represents a sizable fraction of inorganic bromine, as photochemical models predict,[5,7] then this high degree of gas-to-condensed phase partitioning may be arising as a result of the extremely high solubility of HBr in the dilute particles. To better analyze this suggestion requires field experiments that give simultaneous measurements of the partitioning of bromine between the gas and condensed phases, of the relative humidity, and of the aerosol particle composition. The last factor is important, since the solubility of HBr may be even higher in aerosol particles that are somewhat less acidic than pure sulfuric acid.

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