

Reactivity of BrONO₂ and HOBr on sulfuric acid solutions at low temperatures

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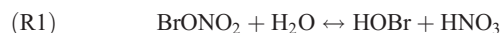
[1] Uptake of BrONO₂ onto bulk sulfuric acid solutions and submicron sulfuric acid aerosol particles was studied in laminar flow cylindrical reactors where a chemical ionization mass spectrometer was used to detect products and reactants. Results from measurements at low temperatures and for sulfuric acid content between 70 and 85 wt.% are presented. These measurements suggest that the reaction probability for BrONO₂ on a given sulfuric acid solution does not depend strongly on temperature. The heterogeneous chemistry of HOBr, a product of the hydrolysis of BrONO₂, was also studied on bulk sulfuric acid solutions (58–70 wt.%). Measurements of HOBr and HNO₃ solubility and the reaction HOBr + HCl → BrCl + H₂O are reported. Supplemented with previous measurements, a set of parameters to calculate the reaction probabilities appropriate to the stratosphere are deduced. These measurements confirm earlier assertions that the reaction can be a significant loss process for HCl when aerosol volume in the stratosphere is elevated. **INDEX TERMS:** 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; **KEYWORDS:** BrONO₂, HOBr, HCl, sulfuric acid

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1. Introduction

[2] The reaction of BrONO₂ + H₂O in/on sulfuric acid aerosol in the atmosphere can lead to significant perturbations of trace atmospheric gases [Hanson and Ravishankara, 1995; Hanson et al., 1996; Lary et al., 1996; Danilin and McConnell, 1995]. For example, at a stratospheric temperature of 210 K and under elevated aerosol loadings, hydrolysis of BrONO₂ can be a significant source of HOBr. The NO₂ “stored” in BrONO₂ can be converted to HNO₃, a more stable NO₂ reservoir species. Subsequent photolysis of HOBr to OH (and Br) can be a significant source of OH at sunrise [Wennberg et al., 1999].

[3] The hydrolysis of BrONO₂,



is a very efficient process as shown in laboratory studies [Hanson and Ravishankara, 1995; Hanson et al., 1996] of the uptake of BrONO₂ by sulfuric acid solutions. Reaction probabilities (γ) of ~ 0.8 were reported for BrONO₂ onto sulfuric acid solutions with H₂SO₄-content between 40 and ~ 70 wt.%. In solutions >75 wt.% H₂SO₄, the value of γ drops off to ≤ 0.1 , a decrease that is related to the diminished water content of these solutions. These measurements were performed primarily near room tem-

perature. In a paper reporting on room temperature measurements of (R1) on sulfuric acid aerosol particles [Hanson et al., 1996], a simple equation relating γ to relative humidity was presented. That equation, however, probably does not accurately describe the γ for (R1) at the low temperatures found in the lower stratosphere (R. Salawitch, personal communication, 1996). Measurements of (R1) on concentrated sulfuric acid at low temperatures are needed to accord a better representation of (R1) in atmospheric models.

[4] In two early studies [Hanson and Ravishankara, 1995; Abbatt, 1995], the physical interaction of HOBr with 60 to 70 wt.% H₂SO₄ was investigated and in separate experiments, HCl was added to solution to study the reaction



The physical solubility measurements indicated that the Henry’s law coefficient for HOBr, H_{HOBr} , was about ten to thirty times that of HOCl. The results from experiments with HCl present, along with H_{HOBr} , led to values for the rate coefficient for (R2) of $\sim 10^5 \text{ M}^{-1} \text{ s}^{-1}$. These studies indicated that when aerosol surface area is high, (R2) could be a significant loss process for HCl. Later measurements reported by Waschewsky and Abbatt [1999] confirm this conclusion and even suggest, albeit subject to an important caveat regarding their results, that under warm (i.e., low

r.h.) stratospheric conditions, HCl loss via (R2) could be significant.

[5] Here, measurements of γ for BrONO₂ hydrolysis, (R1), over a range of sulfuric acid contents and temperatures are reported. Measurements on both bulk solutions and on aerosol particles were performed. In addition, the interaction of HOBr with bulk sulfuric acid solutions was studied. Solubilities for HOBr were measured and in separate experiments reaction probabilities for HCl onto HOBr-doped solutions were measured. Last, the Henry's law coefficients for HNO₃ were also measured.

2. Experimental

[6] Measurements over bulk solutions were performed in a rotating wetted-wall (RWW) flow reactor [Lovejoy *et al.*, 1995; Hanson and Lovejoy, 1996], and the measurements on aerosol particles were conducted in a high-pressure laminar flow reactor, previously described by Lovejoy and Hanson [1995] and Hanson and Lovejoy [1996]. As in the earlier work, a chemical ionization mass spectrometer was used to detect a selection of neutral species exiting the reactors. Brief descriptions of the methods follow; detailed descriptions are provided only for significant changes in the experimental method.

[7] The glass RWW, inner diameter of ~ 1.9 cm \times 14 cm long, rests inside a glass cylindrical reactor (inner diameter of 2.2 cm, reaction zone ~ 15 cm) that is temperature regulated (230 to 295 K) by a flow of thermostatted fluid through a jacket surrounding the reactor. A small amount (0.5 to 2 g) of liquid is placed inside the RWW that is coupled to a stepper motor via a sliding o-ring seal (typical rotation rate of 2 rpm; varied up to 10 rpm.) A small "stir bar" (brass rod encapsulated in glass) was included for the HOBr solubility measurements to provide additional agitation of the liquid. When reactive uptake was investigated, the "stir bar" was not used, except in those cases where gas-phase diffusion was not a significant limiting factor. Carrier gas (He) mass flow rates and pressures ranged from 2 to 6 STP (1 atm, 273 K) cm³ s⁻¹ and 0.4 to 2 torr, respectively. Water vapor partial pressure (0.01 to 0.2 torr) was set by flowing He through or over liquid water in a vessel at a known total pressure and temperature. A reactant was generally introduced to the flow tube through a movable injector (HOBr or BrONO₂ or HCl) or along with the carrier gas (HOBr).

[8] The aerosol experiment consists of an aerosol generator (condensation type), a dilution and mixing volume, an aerosol conditioner to set water content, and a cylindrical flow reactor (3.1 cm inner diameter by ~ 80 cm long.) Both the uptake kinetics of BrONO₂ and the UV spectra of the aerosol particles were measured in the laminar flow reactor [Lovejoy and Hanson, 1995]. The uptake experiments in the aerosol flow tube were carried out at room temperature (295-to-300 K.) Total pressure was typically 160 torr (N₂); mass flow rate and average linear flow velocity were typically 12 STP cm³ s⁻¹ and 6 cm s⁻¹, respectively. The number density of aerosol particles was measured with a condensation-type particle counter and the size distribution parameters were determined from the UV extinction spectra of the aerosol particles [Lovejoy and Hanson, 1995]. Typical particle number densities n_p and size parameters for the

dispersed aerosol (well-described by a lognormal distribution) were: $n_p = 10^5$ to 10^6 cm⁻³, peak radius, $r_p = 0.05$ to 0.5 μ m, and width of distribution, $\log_{10}\sigma = 0.1$.

[9] BrONO₂ was synthesized from BrCl and ClONO₂ according to [Spencer and Rowland, 1978] and stored in a glass trap at dry ice temperatures. During the experiments, the BrONO₂ trap was held at temperatures between 190 and 205 K, and a small flow of He (~ 0.1 STP cm³ s⁻¹) withdrew a small amount of BrONO₂ vapor and this was flowed through the injector. A Teflon plug with a small hole (~ 0.04 cm) was placed downstream of the trap to maintain the total pressure in the trap 15–30 torr higher than that in the flow tube. The CIMS signals (see below) indicated that significant amounts of other species such as HNO₃ and Br₂ were also eluted. [HNO₃] was usually comparable to [BrONO₂]₀ while [Br₂] could be quite large: upon initiating the flow through the trap, it was up to 10 times [BrONO₂]₀. [Br₂] eventually diminished to $\leq 10\%$ (100%) of [BrONO₂] for the bulk (aerosol) experiments. After flowing this dilute BrONO₂ in N₂ mixture through the supply lines for many tens of minutes, [HOBr] and [Br₂O] were usually less than 10% of [BrONO₂]. Concentrations were estimated from the ion signals, the ion-molecule rate coefficients (taken to be 1×10^{-9} cm³ s⁻¹), and the ion-molecule reaction time (~ 0.01 s). Typical initial [BrONO₂] and [HOBr] for the experiments in the RWW were 10^{10} to 10^{11} cm⁻³ while [BrONO₂]₀ was typically 10^{12} -to- 10^{13} cm⁻³ for the aerosol experiments.

[10] For the bulk studies of HOBr solubility and the reaction of HCl with HOBr, HOBr was generated by mixing a small amount of water vapor (a few percent in He at ~ 20 torr total pressure) with the BrONO₂-in-He flow just downstream of the BrONO₂ trap. An additional Teflon plug with a small hole was placed downstream of this section to provide an additional pressure drop between this region and the flow tube.

[11] Detection of BrONO₂, Br₂, HNO₃, HOBr, Br₂O, and HCl was accomplished by reacting a small fraction of these species with the SF₆⁻ reactant ion [Huey *et al.*, 1995; Hanson and Ravishankara, 1995; Hanson *et al.*, 1996] in the CIMS. The resulting product ions (F⁻·BrONO₂, Br₂⁻, F⁻·HNO₃, SF₅O⁻, Br₂O⁻, and for HCl either F⁻·HCl or SF₅Cl⁻, respectively) were monitored. Some of these product ions have the same mass; when Br₂ levels are relatively high, the detection capability for BrONO₂ (F⁻·^{79,81}BrONO₂) decreases due to contributions from ⁷⁹Br⁸¹Br⁻ and ⁸¹Br⁸¹Br⁻. The I⁻ + BrONO₂ \rightarrow NO₃⁻ + IONO₂ reaction was used to monitor BrONO₂ in these circumstances. The I⁻ ion was primarily used in the aerosol experiments as Br₂ levels were generally comparable to BrONO₂.

[12] Reaction probabilities were determined from the observed first-order loss rate coefficients using the standard analysis procedures for flow reactors [Howard, 1979; Brown, 1978]. Gas-phase diffusion, taken into account using the procedure of Brown [1978], is a limiting factor for many of the bulk measurements and the uncertainty of the measured γ can be quite high in this case. The Brown [1978] procedure was also used in the aerosol experiments to obtain the first-order loss rate coefficients k_m from the difference between the first-order loss rate coefficients and the wall loss rate coefficients. The loss rates k_m were converted to extracted reaction probabilities γ_{ex} by dividing

k_m by k_c , the first-order collision rate (k_c is equal to $A\omega/4$ where A is the observed surface area density of the particles and ω is the mean thermal speed of BrONO₂.) The true γ can be slightly larger than γ_{ex} (generally about 10%) because gas-phase diffusion can inhibit the collision rate of the gas with the small particles [Fuchs and Sutugin, 1970; Hanson and Lovejoy, 1996]. γ was obtained from γ_{ex} using the equation of Fuchs and Sutugin [1970]. Further details of this procedure specific to BrONO₂ uptake can be found by Hanson *et al.* [1996] and for the general kinetics of reactions on aerosol particles, Lovejoy and Hanson [1995].

[13] H_{HOBr} was determined by measuring the amount of HOBr taken up by a known volume of solution as described by Donaldson *et al.* [1997] and Hanson and Lovejoy [1996] who measured the solubilities of HOCl and HCl. The results of earlier studies of H_{HOBr} [Hanson and Ravishankara, 1995; Abbatt, 1995; Waschewsky and Abbatt, 1999] depend on the detailed time dependence of the uptake coefficient and an estimated value for the diffusion coefficient of HOBr in solution. The method used here does not depend on these factors; it involves measuring the amount of reactant taken up relative to its equilibrium partial pressure. Neither of those quantities is required to be known on an absolute scale. The amount taken up can also be remeasured by monitoring [HOBr] as it desorbs.

[14] The reaction probability of HCl, γ_{R2} , onto solutions doped with HOBr was measured over a small range of pHOB_r. With the measured H_{HOBr} , the estimated HCl diffusion coefficient (D_1) [Luo *et al.*, 1995; Williams and Golden, 1993; Williams and Long, 1995b], and the Henry's law coefficient for HCl (H_{HCl}^*) [Carslaw and Brimblecombe, 1995; Carslaw *et al.*, 1995b], values for the second order rate coefficient, k^{II} , for (R2) can be obtained using the following equation:

$$\Gamma = (1/\gamma_{R2} - 1/\alpha)^{-1} = \frac{4RTH_{HCl}^* \sqrt{D_1 k^{II} H_{HOBr} p_{HOBr}}}{\omega} \quad (3)$$

α is the mass accommodation coefficient (takes a value of unity [Hanson and Lovejoy, 1996]), p_{HOBr} is the partial pressure of HOBr measured with the CIMS, and ω is the mean thermal speed of HCl. The relative sensitivity of the CIMS for HOBr versus that for HCl was determined using the stoichiometry of (R2) where one HOBr molecule reacts with one HCl molecule. This ratio was 0.6 for detection of HOBr on SF₅O⁻ versus detection of HCl on SF₅³⁵Cl⁻. The calibration procedure of the CIMS for HCl is presented by Hanson [1998].

3. Results and Discussion

3.1. BrONO₂ + H₂O

[15] The results of a typical bulk experiment are shown in Figure 1 where the signals due to BrONO₂ (filled circles and triangles, open squares), HOBr (circles), HNO₃ (+), and ⁷⁹Br⁷⁹Br (open triangles) are displayed as a function of BrONO₂ exposure to a bulk solution containing 79 wt.% H₂SO₄ at 250 K. A small increase in Br₂ (~1 % of the BrONO₂ that was lost) can be seen and is believed to be due to a subsequent reaction of HOBr as discussed below. Both the 79 and 81 isotopes of F⁻ · BrONO₂ are shown (contri-

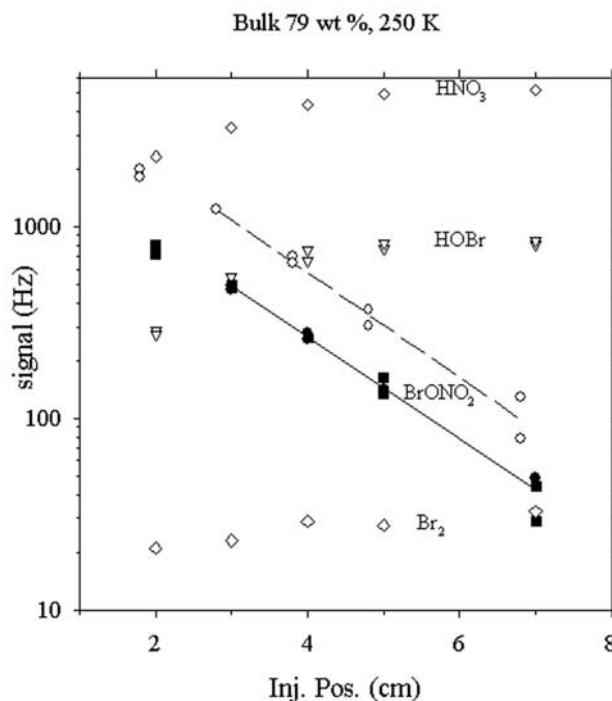


Figure 1. Signals due to BrONO₂ (F⁻ · BrONO₂, filled circles and triangles, NO₃⁻, squares), HOBr (circles), HNO₃ (+), and Br₂ (triangles) as BrONO₂ was exposed to bulk 79 wt.% sulfuric acid liquid at 250 K.

butions from Br₂ and instrument background signals were subtracted), as well as a decay taken with the I⁻ reactant ion (open squares). Least squares fits are shown as the lines through the data (the signals for the 79 and 81 isotopes were averaged) and the slopes of these lines agree to within ±3%.

[16] Typical BrONO₂ loss measurements in the aerosol flow reactor are depicted in Figure 2 where the signal due to BrONO₂ (NO₃⁻) as a function of injector position for two different aerosol samples and in the absence of particles (wall loss) are shown. Temperature was 297 K and the aerosol samples contained ~74 wt.% H₂SO₄ and p_{H2O} for the wall loss measurement was set equal to that of 74 wt.% H₂SO₄.

[17] Figure 3 is a semilog plot of the γ for (R1) measured on bulk (circles) and aerosol particles (triangles) as a function of H₂SO₄ content. The bulk measurements performed at temperatures of 250 ± 10 K are enclosed in boxes (the remaining data were taken at temperatures between 270 to 295 K.) Error bars due to the diffusion correction, a major source of uncertainty, for the data taken over bulk solutions are shown. The scatter in the aerosol data is representative of the uncertainty in these measurements. Also shown (+) are previous measurements on aerosol particles [Hanson *et al.*, 1996].

[18] The γ on bulk solutions as a function of acid-content do not show any significant dependence on temperature from 295 K to 250 K. Therefore, these results indicate that the γ should be represented as a function of H₂SO₄-content. In a model, the H₂SO₄-content of aerosol particles should be calculated from ambient p_{H2O} and temperature [Carslaw *et al.*, 1994, 1995a; Tabazadeh *et al.*, 1997], then γ can be

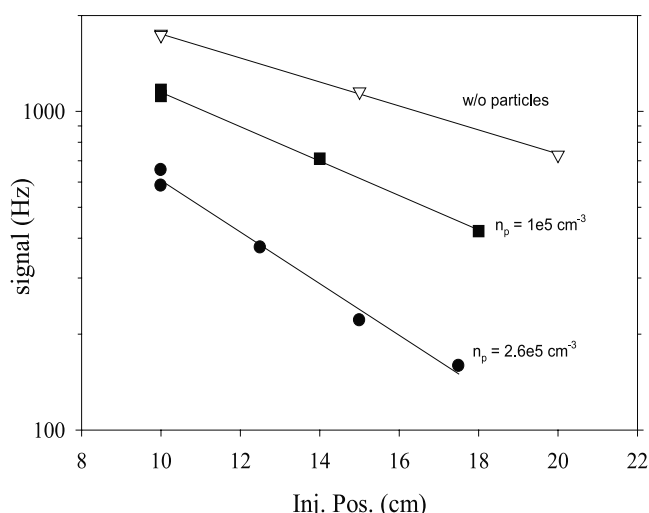


Figure 2. Signal due to BrONO₂ (NO₃⁻) as it was exposed to 74 wt.% sulfuric acid aerosol particles at two number densities (circles, $n_p = 2.6 \times 10^5 \text{ cm}^{-3}$, squares, $n_p = 1.0 \times 10^5 \text{ cm}^{-3}$). A loss measurement in the absence of particles (triangles) to determine the wall loss rate coefficient is also shown. The size distribution of the aerosol particles follow closely a log normal distribution with $r_p = 0.11 \mu\text{m}$ and $\log_{10}\sigma = 0.10$.

calculated from wt.% H₂SO₄ and the fit shown in Figure 3. This fit is of the form

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{1}{\gamma_{rxn}}, \quad \gamma_{rxn} = \exp(a + b \cdot \text{wt.}\%) + \gamma_{100}$$

$$\begin{aligned} \alpha &= 0.80 \\ a &= 29.2 \\ b &= -0.40 \\ \gamma_{100} &= 0.11 \end{aligned} \quad (4)$$

where the values for the parameters were obtained using a least squares fitting routine.

[19] There is a good agreement between the results from the bulk and aerosol measurements. This is an indication that the overall accuracy of the measurement of the kinetics of uptake by aerosol particles is good (see previous verifications of the technique by *Hanson and Lovejoy* [1996], *Lovejoy and Hanson* [1995], and *Hanson* [1998]). The γ s reported here and the previous data [*Hanson et al.*, 1996] are also in good agreement with the exception of the previous $\gamma = 0.05$ data point at 83 wt.%. This previous measurement was probably affected by high [HNO₃]. When pH₂O is low, such as over concentrated (80 wt.%) H₂SO₄ solutions, and pHNO₃ is high, the reverse reaction (R-1) can influence the loss rate determination of BrONO₂. The previous experimental data point at 83 wt.% [*Hanson et al.*, 1996] was not evaluated in terms of the effect of (R-1) (see *Hanson et al.* [1996] for measurements of the thermodynamics of (R1) where ΔH_r° was found to be $1.3 \text{ kcal mol}^{-1}$.) Inspection of Table 1 of *Hanson et al.* reveals that the 83 wt.% experiment had the lowest water partial pressure for which HCl had not been added to scavenge HOBr. A higher than normal HNO₃ partial pressure, probably $\geq 10^{-6} \text{ atm}$, was also likely present during this measurement as the total pressure in the flow reactor was 4 times the typical value. In the present experi-

ments, the amount of HNO₃ present in the aerosol experiments ranged up to $2 \times 10^{12} \text{ cm}^{-3}$ or $\sim 1.5 \times 10^{-7} \text{ atm}$. Some uptake measurements were performed with higher pHNO₃ and the values of γ resulting from these experiments (pHNO₃ ranged from 2.5 -to- $5 \times 10^{-7} \text{ atm}$) fell well below the data shown in Figure 3 (from 20 to 40 % less than the fitted curve.)

[20] Avoiding effects due to the reverse reaction is the main reason the aerosol experiments were performed only at room temperature where pH₂O is high. In the cases where measurements of γ at low pH₂O are desired, the bulk measurements should be reliable because they were much less influenced by (R-1) due to the ~ 100 -fold reduction in HNO₃ levels compared to the aerosol experiments. The γ for (R1) in these situations (0.1 to 0.2) are in a range of values over which they can be measured with an accuracy of $\pm 40\%$ or better.

[21] Because of the high reactant concentrations in the aerosol experiments, secondary reactions involving HOBr are complicating factors in the BrONO₂ loss measurements, especially at high acid content when pH₂O is low. In strong acids ($> \sim 80 \text{ wt.}\%$), some Br₂ was formed as the BrONO₂ was lost; it appears that HOBr was transformed to Br₂ via secondary reactions. Reaction of BrONO₂ with product HOBr is a possibility; however, if it is a direct reaction producing Br₂ the coproduct should be HO₂NO₂, which was not detected. Further evidence that the Br₂ is not produced via secondary reactions involving BrONO₂ is shown in Figure 4, a plot of the signals from an experiment where neat HOBr was repeatedly exposed to a bulk 80 wt.%

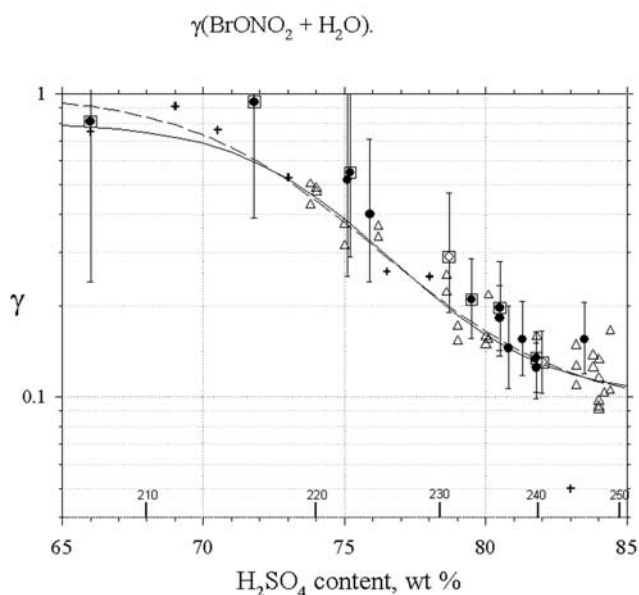


Figure 3. Measured reaction probabilities for uptake of BrONO₂ onto sulfuric acid plotted versus acid content. Measurements on bulk liquids measured here are the filled circles and temperature was varied from 240 to 293 K (those enclosed by squares are measurements taken at $250 \pm 10 \text{ K}$). Measurements on aerosol particles measured here are plotted as triangles and previous measurements [*Hanson et al.*, 1995] are plotted as +.

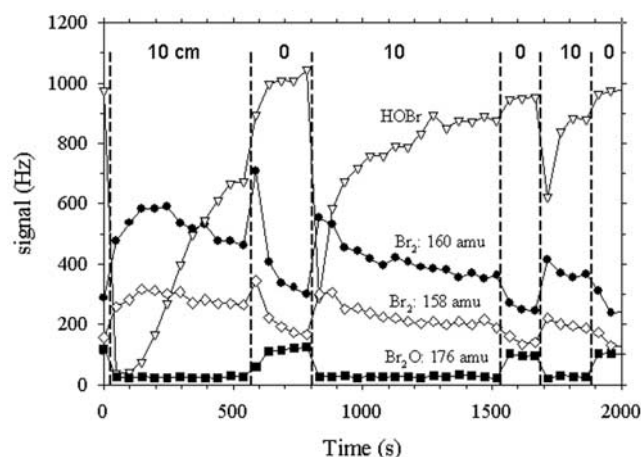
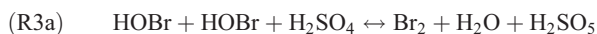
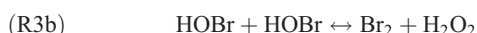


Figure 4. Variation of the signals due to HOBr (triangles) and Br₂ (circles and diamonds) as HOBr was repeatedly exposed to an 80 wt.% sulfuric acid solution.

H₂SO₄ solution. As HOBr was exposed to the acid (delineated by the vertical dashed lines; marked as 10 cm when exposed), the Br₂ signals increase. The integrated amount of Br₂ that was produced is roughly matched ($\pm 30\%$) by the integrated amount of HOBr that was lost. This estimate is based on the relative yields of HCl and Br₂ produced in the reaction of $\text{HBr} + \text{BrCl} \rightarrow \text{Br}_2 + \text{HCl}$ [Hanson and Ravishankara, 1992] and the relative sensitivities for HOBr and HCl found here. The initial large uptake of HOBr is probably due to oxidation of small amounts of impurities in the acid, an effect also noted for HOCl [Donaldson *et al.*, 1997]. The amount of HOBr that was converted to Br₂ decreases with exposure time indicating that [impurity] apparently decreased with time. Note that for long exposures, a noticeable amount of Br₂ was still being produced. This may be due to a process that is slower than what was responsible for the Br₂ production at short times. The initial impurity may act to speed up the conversion of 2 HOBr molecules to a Br₂ molecule and its efficacy in this respect decreases as it becomes oxidized. Further conversion to Br₂ may also occur if the H₂SO₄ or HSO₄⁻ species are oxidized to H₂SO₅ or HSO₅⁻, which upon reaction with H₂O, leads to H₂O₂. The overall reaction might be represented as either



or



(R3b) is slightly endothermic, $+1.6 \text{ kcal mole}^{-1}$ (gas-phase value [DeMore *et al.*, 1992]), which is a value similar to that for (R1). Based on thermodynamics, (R3a) or (R3b) might occur in these experiments. Whether or not (R3a) or (R3b) represents the overall reaction, the Br atoms in Br₂ are derived from HOBr, thus the rate of the process is probably second order in HOBr. At the much higher [HOBr] in the aerosol experiments, this conversion of HOBr into Br₂ will be more efficient, as was observed.

3.2. HOBr Solubility

[22] The solubility of HOBr was studied in 58 to 70 wt.% H₂SO₄ solutions at temperatures from 250 to 270 K. A plot of HOBr signal versus time is shown in Figure 5 as HOBr was twice exposed then not exposed to a 66 wt.% H₂SO₄ solutions at 250 K. The solubility of HOBr was calculated from A_i (dimensionless), the average of the integrated uptake and desorption areas, i.e., the departure of the HOBr signal from the unperturbed HOBr signal, S_0 , (s^{-1} , dashed line) according to

$$H_{\text{HOBr}} = \frac{A_i}{S_0} \frac{V_{\text{car}}}{v_{\text{liq}}} \frac{1}{RT} \quad (5)$$

V_{car} is the volume flow rate of the He carrier gas ($\text{cm}^3 \text{ s}^{-1}$), v_{liq} is the volume of the liquid (cm^3), R is the gas constant, and T is temperature [Hanson and Lovejoy, 1996]. Small corrections were made to the integrated areas due to Br₂ and BrCl production and Br₂O loss. The variations of these species with exposure to the acids was only a few percent of [HOBr]₀, however, over the course of the 300 to 600 s exposures, the corrections to A_i amounted to up to 25%. As it is not certain that loss of Br₂O leads to HOBr production or that Br₂ production resulted from HOBr secondary reactions, the uncertainty in the measured values is assigned to be $\pm 50\%$ ($\pm 25\%$ precision along with the 25% possible systematic error due to the corrections). Finally, HNO₃ was monitored to provide a check for the measurements and values for H_{HNO_3} are reported here. Note that [HNO₃] was less than or equal to 10^{10} cm^{-3} in these experiments ($\text{pHNO}_3 < 5 \times 10^{-10} \text{ atm}$) which, coupled with the pH_2O of $\geq 3 \times 10^{-5} \text{ atm}$, ensures that conversion of HOBr to BrONO₂ will be negligible ($< 0.01\%$).

[23] Shown in Figure 6 are the 250 K results of the solubility measurements of HOBr (solid circles) and HNO₃ (triangles) as a function of wt.% H₂SO₄. According to these results, H_{HOBr} is independent of acid content over the range 58 to 70 wt.% H₂SO₄. This is not surprising as it was found that H_{HOCl} [Donaldson *et al.*, 1997] also does not vary

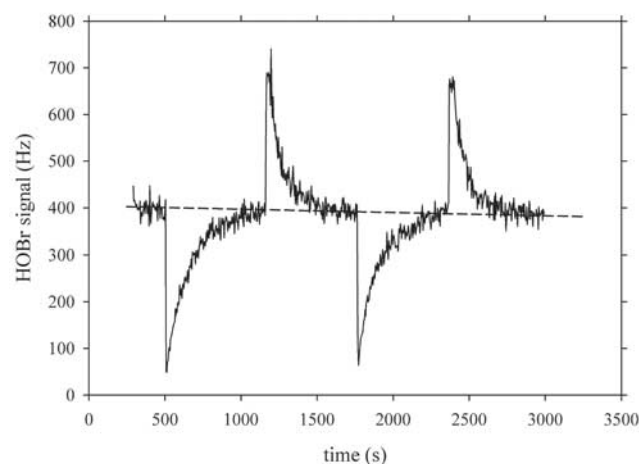


Figure 5. HOBr signal versus time as HOBr was twice absorbed then desorbed from a 66 wt.% H₂SO₄ solution.

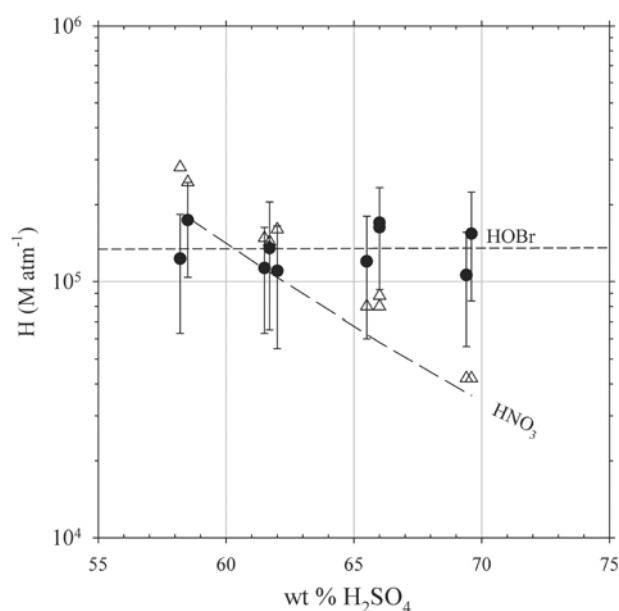


Figure 6. Solubilities extracted from experiments such as that shown in Figure 5 plotted versus acid content. H_{HOBr} (circles) and H_{HNO_3} (triangles) from the present work and model-generated [Carslaw and Brimblecombe, 1995; Carslaw et al., 1995a, 1995b] H_{HNO_3} (dashed line) are shown.

strongly with sulfuric acid content over this range (from 1.7×10^3 to 1×10^3 M atm⁻¹). The independence of H_{HOBr} with acid content was also reported by Waschewsky and Abbatt [1999]. However, extrapolation of their data to 250 K (they report measurements from 208 to 238 K) results in a value for H_{HOBr} of 3×10^4 M atm⁻¹, much lower than the average of the values shown in Figure 6 of 1.4×10^5 M atm⁻¹. The H_{HNO_3} reported here vary with acid content as given by a model [Carslaw and Brimblecombe, 1995; Carslaw et al., 1995a, 1995b] (dashed line), however, the absolute values reported here are larger than the model values by about 35%.

[24] In some experiments, S_0 was not easy to identify in that the uptake and desorption asymptotic signal levels were greater than 10% different. In these cases, variations in Br₂ etc. were on the order of 5% of S_0 , significantly larger than in the well-behaved solubility experiments. The values of H_{HOBr} from these experiments were much lower than the well-behaved experiments, 50-to-70% lower. In most of these cases, the common experimental parameter was a relatively high level of HOBr, about a factor of two higher than the other experiments (typical pHOBr of $\sim 10^{-10}$ atm). This indicates that secondary reactions transforming HOBr into unmonitored Br compounds may have taken place. Earlier researchers also report [Waschewsky and Abbatt, 1999] erratic behavior in their solubility measurements when pHOBr was relatively high ($\sim 3 \times 10^{-9}$ atm or higher.) One experiment here where an acid sample had come into contact with a metal tweezers resulted in a value of H_{HOBr} that was about twice the other experiments. The explanation for this behavior is not understood.

[25] The temperature dependence of H_{HOBr} and H_{HNO_3} was also studied. Shown in Figure 7 are the results from

experiments performed between 270 and 250 K for 66 wt.% acid content where the H_{HOBr} and H_{HNO_3} are plotted in a semilog plot versus $1/T$. The slope of a least squares fitted line gives a value for the enthalpy of solvation for HOBr of $-12.5 (\pm 3.7, 95\% \text{ confidence level})$ kcal mol⁻¹. This heat of solvation is greater than that reported by Waschewsky and Abbatt of $-9 (\pm 1, 1\sigma)$ kcal mol⁻¹, but they are not in disagreement, considering the error bars at the 95% confidence level. Note that if the present data is extrapolated to 222 K, near the middle of the temperatures reported by Waschewsky and Abbatt, the value of H_{HOBr} is about 11 times their value. The value obtained via extrapolation of the 95% confidence level line is about 4 times their value. Finally, the H_{HNO_3} vary as expected with acid content, although they take values slightly larger than the values given by the Carslaw model [Carslaw and Brimblecombe, 1995; Carslaw et al., 1995a, 1995b] (dotted line), resulting in an average deviation of 30%, a deviation similar to that found for the variation with acid content at 250 K.

3.3. Reaction of HCl With HOBr Doped Solutions

[26] HOBr was introduced with the carrier gas and allowed to saturate a liquid film whereupon HCl, entering through the injector, was reacted with it. Experiments were conducted for sulfuric acid solutions of 58 to 70 wt.% at 250 K and pHOBr ranged from 2×10^{-10} to 2×10^{-9} atm. It is likely that HOBr follows Henry's law at these higher pressures even though performing measurements of H_{HOBr} at these high pHOBr are problematical.

[27] The results of the measurements are shown in a log plot (Figure 8) as Γ versus pHOBr. Γ has been extricated from the measured γ by separating out the mass accommodation coefficient α via equation (3) with $\alpha = 1$. The data should follow a line that has a slope of $\frac{1}{2}$ and it can be seen that they in general do. The slopes range from 0.55 to 0.65; a slope slightly higher than 0.5 might indicate a contribution from a potential surface reaction [Hanson, 1997, 1998;

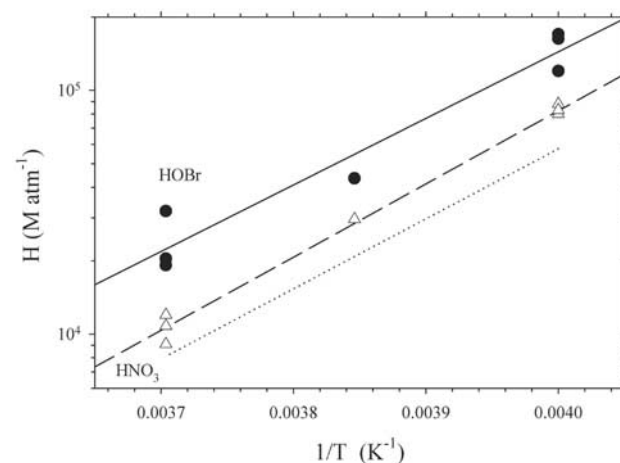


Figure 7. HOBr (circles) and HNO₃ (triangles) solubilities measured here are plotted versus inverse temperature. Also shown are model-predicted values for H_{HNO_3} [Carslaw and Brimblecombe, 1995; Carslaw et al., 1995a, 1995b] (dotted line).

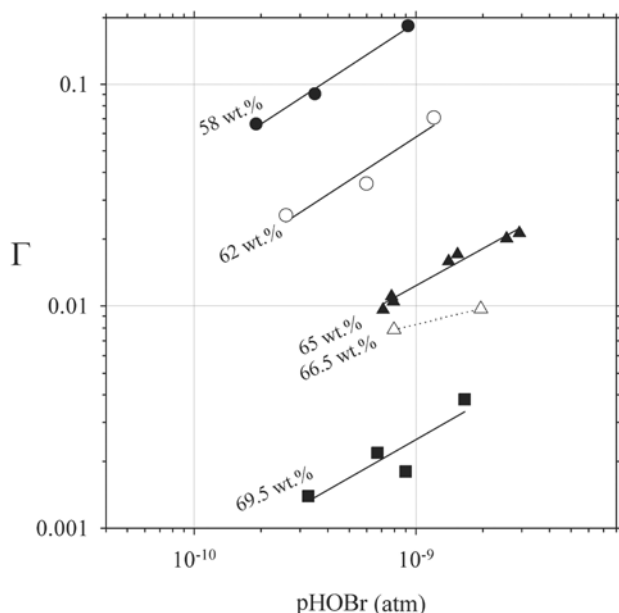


Figure 8. Reaction probability for HCl due to (R2) is plotted versus pHOBBr. Γ_{HCl} is the bulk reaction probability that has been separated from α . Measurements were conducted at 250 K onto bulk solutions (H_2SO_4 -content is indicated in the figure.)

Hanson and Ravishankara, 1994]. For simplicity in deriving the rate coefficient for (R2) in bulk solution, it is assumed that the contribution of the surface reaction is negligible. The measurements of (R2) by Waschewsky and Abbatt [1999] are consistent with this assumption. The lines are fits according to

$$\Gamma = a\sqrt{p\text{HOBBr}}, \quad a = bH_{\text{HCl}}^* \sqrt{D_1 k^{\text{II}} H_{\text{HOBr}}}, \quad (6)$$

$$b = 4RT/\omega = 2.13 \times 10^{-3}$$

The second relation comes from (3) and shows the relation between the parameter a and H_{HCl}^* , D_1 , H_{HOBr} , and k^{II} . Shown in Table 1 are the values of a for each acid content, the physical parameters, and the extracted k^{II} . The solubility of HOBr was taken from the present data with a value of $1.4 \times 10^5 \text{ M atm}^{-1}$ and was assumed to be independent of H_2SO_4 -content.

[28] Recent measurements [Behr et al., 2001] of H-D exchange for HCl uptake onto D_2SO_4 indicate that the overall solubility of HCl-like species (HCl , Cl^- , ClSO_3^-) in 65 to 70 wt.% sulfuric acid solutions is much greater than that given by the H_{HCl}^* of Carslaw et al. (the ones used here.) This enhanced solubility [Behr et al., 2001] may be due to formation of chlorosulfonic acid (ClSO_3H and ClSO_3^-) [Robinson et al., 1998]. In what follows, it is assumed that this is so and that reaction of HOBr with this species is negligible compared to reaction with Cl^- . Then the value of k^{II} depends on how well the H_{HCl}^* of Carslaw and Brimblecombe [1995] and Carslaw et al. [1995a, 1995b] predicts the correct level of $[\text{Cl}^-]$ for sulfuric acid contents up to 70 wt.%.

[29] Shown in Figure 9 are the k^{II} versus wt.% H_2SO_4 along with the diffusion limited second order rate coefficient

[Atkins, 1990] with the capture radius, R^* , set to 1 nm, i.e., that applicable to an ionic reaction in solution. The extracted k^{II} are well below the diffusion limited values. Consideration of the uncertainties in the extracted k^{II} (on the order of $\pm 3 \times 3$ [Hanson and Ravishankara, 1995; Abbatt, 1995; Waschewsky and Abbatt, 1999]), however, indicates that the 70 wt.% k^{II} could be near the diffusion-limited value. Waschewsky and Abbatt [1999] report k^{II} for similar acid content at temperatures of 213, 228, and 238 K. Their values for k^{II} in 70 wt.% acid significantly exceed the diffusion limited value for $R^* = 1 \text{ nm}$. They point out that this comparison could be affected by the uncertainty in the solubility of H_{HCl}^* upon which k^{II} depends quadratically. In addition, the H_{HOBr} reported here are significantly larger (a factor of 3 to 10) than they report. If they were to use a 3-to-10 times larger H_{HOBr} , their k^{II} would fall at or below the diffusion limited values.

[30] Also shown in Figure 9 as the dotted line are the second order rate coefficients for $\text{HOCl} + \text{HCl}$ at 250 K from Donaldson et al. [1997]. The k^{II} presented here suggest that (R2) is substantially faster than the equivalent reaction involving HOCl, however, it is much less dependent, nearly independent, of acid content. The k^{II} reported by Waschewsky and Abbatt at 213 K exhibit a strong acid content dependence. However, at 228 K this dependence is lessened and at 238 K it is even further decreased. Therefore, a low dependence on acidity at higher temperature is consistent with the trends in their data.

3.4. Temperature Dependence of k^{II}

[31] Previous measurements [Hanson and Ravishankara, 1995; Abbatt, 1995; Waschewsky and Abbatt, 1999] of the rate coefficient for (R2) in 60 wt.% H_2SO_4 have been reported at 210, 218, and 228 K. Shown in Figure 10 is $\log k^{\text{II}}$ versus $1/T$ for these data at 60 wt.% and the current measurement at 58 wt.%. The line is a least squares fit and the slope yields an activation energy for (R2) of 15 kcal mol^{-1} . Recall that the earlier data (including Hanson et al. [1995]) were obtained using H_{HOBr} that may be low by a factor of up to 10. The reported k^{II} would be corrected downward if H_{HOBr} were to be revised upwards. This is shown as the open symbols where the values of k^{II} at 228, 213, and 210 K have been divided by factors of 6.7, 8, and 10, respectively (see below.) An increased dependence on temperature for k^{II} is apparent. It seems that an activation energy of 15 kcal mol^{-1} or higher is characteristic of (R2) in $\sim 60 \text{ wt.}\% \text{ H}_2\text{SO}_4$ solution. This is quite a bit higher than the value of $\sim 6 \text{ kcal mol}^{-1}$ [Donaldson et al., 1997] found for $\text{HOCl} + \text{HCl}$.

Table 1. Parameters Used to Extract k^{II} for the Heterogeneous Reaction $\text{HCl} + \text{HOBr} \rightarrow \text{BrCl} + \text{H}_2\text{O}$ at 250 K^a

wt.% H_2SO_4	a	H_{HCl}^* [18], M/atm	D_1 [16], cm^2/s	k^{II} , $\text{M}^{-1} \text{s}^{-1}$
58	5600	1740	$6.6\text{e}-7$	$2.5\text{e}7$
62	1630	400	$5.4\text{e}-7$	$4.8\text{e}7$
65	400	130	$4.4\text{e}-7$	$3.3\text{e}7$
66.5	240	70	$4\text{e}-7$	$4.6\text{e}7$
69.5	75	22	$3\text{e}-7$	$6\text{e}7$

^aThe rate coefficient was calculated from $k^{\text{II}} = (a/(bH_{\text{HCl}}^*))^2 (D_1 H_{\text{HOBr}})^{-1}$ where $b = 4RT/\omega = 2.13 \times 10^{-3}$ and $H_{\text{HOBr}} = 1.4 \times 10^5 \text{ M atm}^{-1}$.

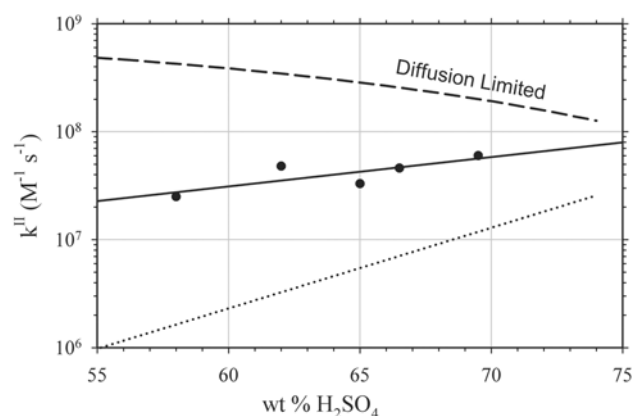


Figure 9. Second order rate coefficient for (R2) extracted from the measurements presented here plotted versus wt.% H₂SO₄. Dashed line is the diffusion limited second order rate coefficient and the dotted line is k^{II} for HOCl + HCl [Donaldson *et al.*, 1997].

[32] Waschewsky and Abbatt report activation energies much less than this (~ 10 kcal mol⁻¹) in 66 and 70 wt.% H₂SO₄ solutions for temperatures below 228 K. However, their measurements at 238 K did not show an increase in k^{II} over the 228 K data that was commensurate with that high of an activation energy. These changes in activation energy with temperature and acid content could represent a change in the mechanism for (R2). This conjecture would need to be tested through additional experimental investigations.

[33] The current measurements of H_{HOBr} and those of Waschewsky and Abbatt [1999] are between a factor of 4 and 10 different. This range of factors is due to the extrapolation in temperature needed to compare the data and the uncertainty in the solvation enthalpy. The average of the solvation enthalpies reported by Waschewsky and Abbatt [1999] and the present work can be used (-10.8 kcal mol⁻¹) to extrapolate the present data set to temperatures of 238, 228, and 213 K. This results in values that are different from that of Waschewsky and Abbatt by factors of 6, 6.7, and 8, respectively. Finally, multiplying the H_{HOBr} of Hanson and Ravishankara [1995], also obtained using the $H(\text{D})^{1/2}$ method, by a factor of ten will bring it into accord with the present data extrapolated to 210 K.

[34] Choosing which set of H_{HOBr} to use as the true values is difficult. Both sets of data reveal that H_{HOBr} is not dependent on acid content and both have similar temperature dependencies. The quantitative differences may be due to some unidentified chemistry and/or differences in the experimental technique. Note that the equilibration technique used here is recognized [Carslaw and Brimblecombe, 1995; Carslaw *et al.*, 1995a, 1995b; Hanson, 1998; Hanson and Lovejoy, 1996] as more reliable than the time dependent approach employed by Hanson and Ravishankara [1995], Abbatt [1995], and Waschewsky and Abbatt [1999]. While the details of the time-dependency of the signal are needed to determine $H(\text{D})^{1/2}$, the equilibration technique used here does not depend on such. Small errors in determining the baseline signal level have a large impact on results from the $H(\text{D})^{1/2}$ technique. In addition, an estimate for the value of D is necessary. Furthermore, the theory behind the $H(\text{D})^{1/2}$ technique requires that the gas-phase concentration of the

solute remain constant with time [Danckwerts, 1970], a condition that can only be approximated in an experiment, particularly when the solubility is large. In the discussion that follows, the values from the present work are taken to be H_{HOBr} .

[35] This choice of H_{HOBr} allows one to arrive at a coherent set of k^{II} as a function of T and wt.% H₂SO₄. Shown in Figure 11 are the k^{II} from the current and previous work [Waschewsky and Abbatt, 1999] as a function of H₂SO₄ wt.%. The previously reported values of k^{II} have been divided (to keep the product $H_{\text{HOBr}}k^{\text{II}}$ constant) by the factors discussed above. There seems to be a consistent picture of the variation of k^{II} with temperature and H₂SO₄-content. The treatment also yields values for k^{II} in 70 wt.% acid that are equal to or less than the diffusion limited rate coefficients. However, the observed dependence of k^{II} on temperature and wt.% is difficult to explain. Understanding the types of chlorine species that might be present [Behr *et al.*, 2001; Robinson *et al.*, 1998] and how they change with acid content and temperature might lead to a better description for the rate coefficient of reaction (2).

3.5. HOBr + HCl in Stratospheric Sulfuric Acid Aerosol

[36] Shown in Table 2 are the parameters that determine the reaction probability γ for HOBr + HCl for stratospheric conditions. The reaction probability for HCl is given by

$$\gamma = \left(\frac{1}{\alpha} + \frac{1}{f(l/r)\Gamma} \right)^{-1}, \quad \Gamma = \frac{4RTH_{\text{HCl}}^*\sqrt{D_l k^{\text{I}}}}{\omega},$$

$$k^{\text{I}} = k^{\text{II}} H_{\text{HOBr}} p_{\text{HOBr}} \quad (7)$$

where $f(l/a) = \coth(r/l) - l/r$ is a factor [Hanson *et al.*, 1994] that takes into account the finite size of the particles of

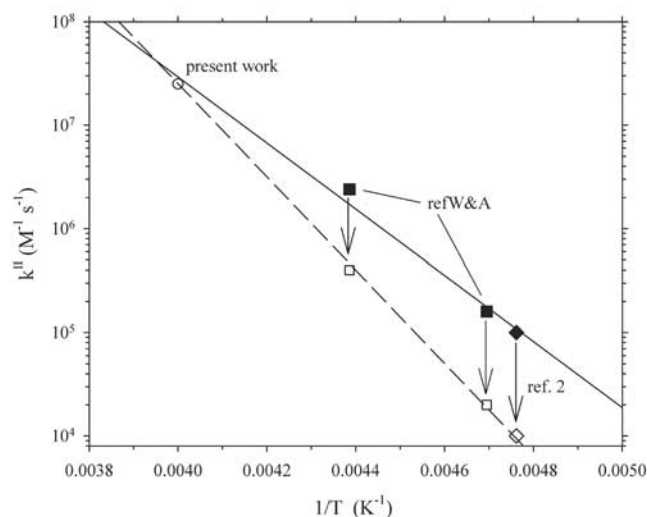


Figure 10. k^{II} for (R2) in 59 ± 1 wt.% H₂SO₄ as a function of inverse temperature. Present work (circle), Hanson *et al.* [1995] and Waschewsky and Abbatt [1999] (solid diamond and solid squares, respectively), those of Hanson *et al.* [1995] and Waschewsky and Abbatt [1999] with corrections applied as detailed in text (diamond and squares, respectively.)

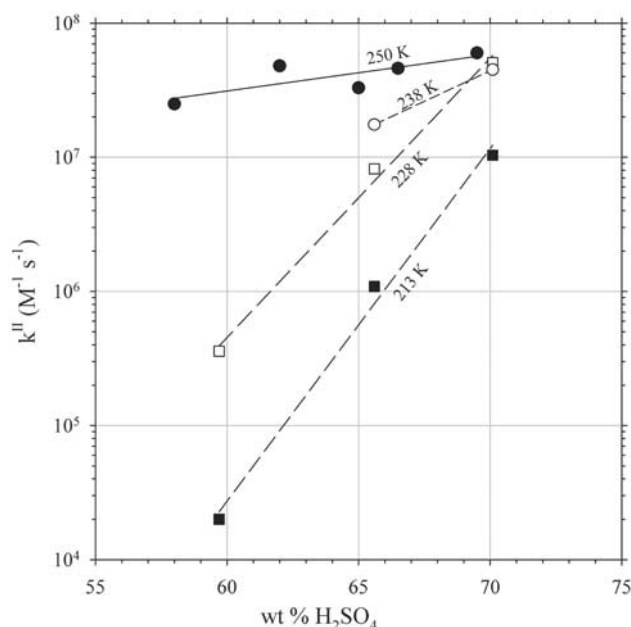


Figure 11. k^{II} for (R2) is plotted versus wt.% H_2SO_4 . Present work at 250 K (filled circles), those of *Waschewsky and Abbatt* [1999] (238 K: circles, 228 K: squares, 213 K: filled squares) with corrections as detailed in the text.

radius r and $l = (D_1/k^{\text{I}})^{1/2}$. Using a heat of solvation of $10.8 \text{ kcal mol}^{-1}$ and the average value of H_{HOBr} reported here at 250 K, the solubility of HOBr is given by

$$H_{\text{HOBr}} = \exp(-9.86 + 5427/T) \quad (8)$$

It is assumed that H_{HOBr} does not vary with acid content over the range 60 to 70 wt.% H_2SO_4 , in accord with the results presented here and by *Waschewsky and Abbatt* [1999]. The second order rate coefficient for (R2) varies with acid content and temperature in a very complicated manner (Figure 11): a very strong temperature dependence is observed in 60 wt.% acid while it is much weaker in 66 and 70 wt.% acid. Values for k^{II} for stratospheric conditions were obtained by fitting an equation of the form

$$k^{\text{II}} = \exp(a + bW) \exp(-(c + dW)/T), \quad \begin{aligned} a &= 154, b = -1.63 \\ c &= 38,500, d = -478 \end{aligned} \quad (9a)$$

$$k_{\text{dl}} = 7.5 \times 10^{14} (D_1/\text{cm}^2 \text{ s}^{-1}) (R^*/\text{nm}) \quad (9b)$$

with W the H_2SO_4 -content in wt.%. The diffusion limited rate coefficient [Atkins, 1990], (9b), is approximately $1.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for a value of $D_1 = 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ typical of stratospheric aerosol and for $R^* = 2 \text{ nm}$. Equation (9a) reproduces the values of k^{II} at 213 and 228 K shown in Figure 11 to an average deviation of 20%. It overestimates those at 238 K by up to a factor of 3 and those at 250 K by up to a factor of 6 so one must proceed carefully before using this equation at high temperatures or for acid content

$< \sim 55 \text{ wt.}\%$. The equation for k^{II} can exceed k_{dl} and thus k_{dl} should be imparted as an upper limit to k^{II} .

[37] Waschewsky and Abbatt point out that the concentration of HCl can exceed that of HOBr in dilute sulfuric acid solutions and/or when [HOBr] is low. However, this does not need to be taken into account as the reaction goes over completely to the volume limit in these dilute solutions. For example, from Table 2, the reacto-diffusive length l_{HCl} in 60, 66, and 70 wt.% acid is $\sim 6, 0.6$, and $0.17 \mu\text{m}$, respectively. The value of l in the 60 and even the 66 wt.% solutions are greater (those for HOBr are larger yet) than the typical “midpoint” radii of aerosol in the stratosphere, even during elevated loadings, indicating that the reaction can be treated as a volume reaction. Note that this is explicitly taken into account in equation (7).

[38] Shown in Figure 12 are the HCl reaction probabilities due to (R2) (two different calculations are shown, see below), that for reaction with ClONO_2 [Hanson, 1998] and that for reaction with HOCl [Donaldson et al., 1997]. $p\text{ClONO}_2$ was taken to be $2.5 \times 10^{-11} \text{ atm}$ [DeMore et al., 1992] and $p\text{HOCl}$ was taken to be $2 \times 10^{-12} \text{ atm}$ (these are representative values at 20 km altitude near the south pole in the spring and fall, D. Kinnison, private communication, 2002). The HCl γ s for (R2) were calculated two ways: (1) with k^{II} according to equations (9a) and (9b) and (2) according to equation (10). For approach (2), the k^{II} of Waschewsky and Abbatt was used but its value was divided by a factor of 8 to compensate for the increase in H_{HOBr} used here (so that the measured value for the product $k^{\text{II}}H_{\text{HOBr}}$ is kept constant.)

$$k^{\text{II}} = 3700 \exp(0.542W - 6440/T) \quad (10)$$

In both cases, equations (7) and (8) and the H_{HCl}^* of Carslaw et al. were used. For sulfuric acid solutions more dilute than $\sim 63 \text{ wt.}\%$ as would be found at certain times at upper latitudes, there is a significant difference in the calculated γ s for (R2). At this point, however, HCl loss due to reaction with ClONO_2 (and possibly HOCl) begins to be dominant, so this difference may not be consequential.

[39] The γ in Figure 12 were calculated for a typical background stratospheric aerosol that has a volume weighted average radius of $\sim 2 \times 10^{-5} \text{ cm}$. As shown by Waschewsky and Abbatt [1999] for a surface area of $10^{-8} \text{ cm}^2/\text{cm}^3$ and a reaction probability of 10^{-4} , only a few tens of molecule $\text{cm}^{-3} \text{ s}^{-1}$ of HCl are converted to photolabile BrCl . However, if the sulfuric acid layer becomes perturbed

Table 2. γ_{HCl} Due to (R2) for Uptake Onto Particles With $r = 0.2 \mu\text{m}$ and Stratospheric Conditions of $p\text{HOBr} = 5 \times 10^{-13} \text{ atm}$ and $p\text{HCl} = 5 \times 10^{-11} \text{ atm}$

$T, \text{ K}$	wt.% H_2SO_4	$H_{\text{HOBr}}, \text{ M/atm}$	$H_{\text{HCl}}^*, \text{ M/atm}$	$k^{\text{II}}, \text{ M}^{-1} \text{ s}^{-1}$	$l_{\text{HCl}}, \mu\text{m}$	$l_{\text{HOBr}}, \mu\text{m}$	γ_{HCl}
214	70	5.4e6	230	1.3e7	0.17	2.4	1.3e-4
208	66	1.1e7	1000	4.4e5	0.6	6.4	1e-4
201	60	2.8e7	7e4	1.5e3	6	13	3e-5

^aThe diffusion coefficient for HCl of $\sim 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ is nearly independent of stratospheric conditions [Luo et al., 1995; Williams and Golden, 1993; Williams and Long, 1995]. D_1 for HOBr is taken to have the same value as that for HOCl [24]. Note that the reaction probabilities are not dependent on the value of D_1 for radii $\leq 0.2 \mu\text{m}$.

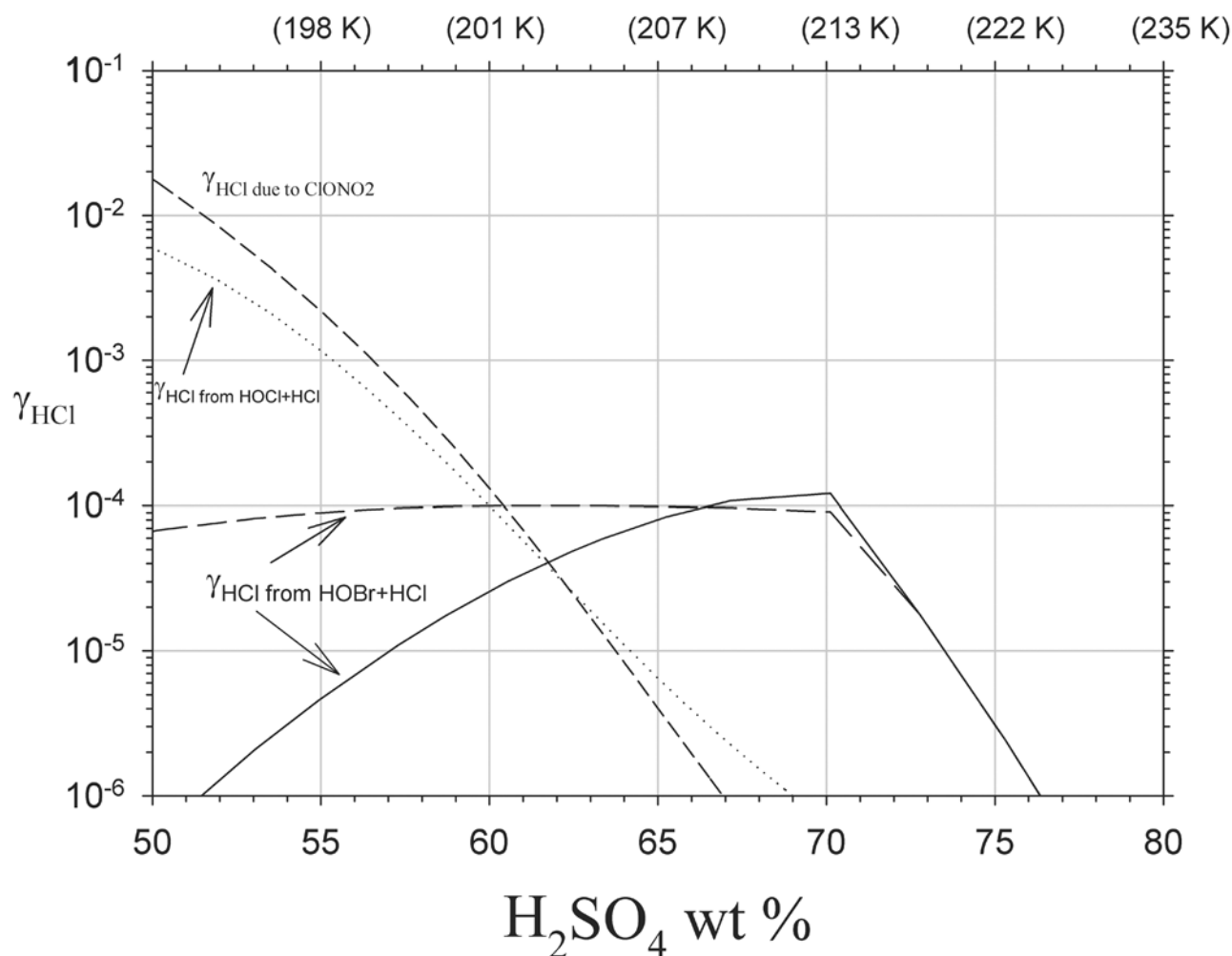


Figure 12. Reaction probability for HCl is plotted versus wt.% H₂SO₄ for a variety of reactions for stratospheric conditions. The temperature that a particle will contain the indicated H₂SO₄ is shown at the top of the graph. Two different formulations (9a) and (10) of the k^{II} for HOBr + HCl were used to generate the two different curves for this reaction. In both cases, the value of k^{II} was constrained to be less than the diffusion-limited value (9b) See text for details.

due to a volcanic eruption, surface area can increase to 20-to-50 times background (particle volume increases can be even greater causing the reaction probability for (R2) to increase). Then loss of HCl due to (R2) can be several hundred molecule $\text{cm}^{-3} \text{s}^{-1}$ which is a significant loss compared to the gas-phase reaction of OH with HCl.

[40] The efficacy of (R2) is predicted to decrease precipitously for acid contents greater than 70 wt.%. This decrease is due to the reaction rate becoming diffusion limited. The solubility of HCl is very small in these solutions and has not been adequately studied in the laboratory. Furthermore, it is not clear how accurate the model-generated values [Carslaw and Brimblecombe, 1995; Carslaw et al., 1995a, 1995b] of this quantity are in these concentrated solutions [Behr et al., 2001; Robinson et al., 1998]. More accurate H_{HCl}^* will lead to alterations in k^{II} , the reacto-diffusive length l , and the reaction probability. This might lead to significant changes in the calculated γ_{R2} for small particles with acid content ≥ 70 wt.%. H_{HOBr} has also not been reported for these solutions. It seems that further studies of this reaction in strong acid solutions are warranted. If γ_{R2}

were to attain values of 10^{-4} or higher in particles with H₂SO₄-contents up to 80 wt.%, then a significant role for (R2) in volcanic conditions may extend up to 235 K.

[41] **Acknowledgments.** The measurements were carried out at the Aeronomy Laboratory, part of the National Oceanic and Atmospheric Administration while the author was affiliated with the Cooperative Institute for Research in Environmental Sciences, University of Colorado. Comments on the manuscript by J. J. Orlando, stratospheric model data from D. Kinnison, and conversations with R. J. Salawitch are gratefully acknowledged.

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