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HONO Solubility and Heterogeneous Reactivity on Sulfuric Acid Surfaces

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The solubility of HONO in various wt % sulfuric acid solutions was measured. HONO becomes increasingly more soluble in high acid wt % solutions, probably resulting from the protonation of HONO to give H_2ONO^+, followed by dissociation and association to give $NO^+HSO_4^-$ (nitrosyl sulfuric acid). The reaction of HONO with HCl on 50, 60, 67, and 70 wt % sulfuric acid solutions was also studied. The measured uptake coefficients could not be explained simply by the occurrence of a bulk phase reaction, and a surface effect is found to contribute to the uptake. The reaction of HONO with HCl was measured on sulfuric acid particles, and a small reacto-diffusive length further supports a surface reaction. From extrapolating our measured uptake values to stratospheric conditions, the formation of ClNO from the heterogeneous reaction of HONO and HCl is concluded to be an insignificant process in the volcanically unperturbed stratosphere.

Introduction

Heterogeneous activation of chlorine by polar stratospheric clouds is a well-documented phenomena[1,2] and has been extensively studied by field campaigns[3] and in the laboratory.[4] In the extrapolar mid to lower stratosphere (15−25 km), sulfate aerosols of 60−80 wt % sulfuric acid are the predominant heterogeneous surfaces[5] and the heterogeneous activation of chlorine is thought to be much less efficient.[6] For example, reactions such as $ClONO_2 + HCl$ and $HOCl + HCl$ can occur in sulfuric acid, but their efficiencies decrease considerably as temperatures warm above ∼210 K; consequently, their contributions to chlorine activation at midlatitudes is minimal.[6]

Burley and Johnston[7] suggested that nitrosyl sulfuric acid (NSA, formula $NOSO_4H$) could be readily formed in sulfuric acid aerosol in the stratosphere and that reaction of NSA with dissolved HCl (or Cl^-) could yield ClNO. ClNO, once in the gas phase, is readily photolyzed; thus, the proposed scheme results in activation of chlorine. The formation of NSA is favored in more concentrated sulfuric acid (thus warm atmospheric temperatures), and reaction of HCl with NSA might be a source of active chlorine at midlatitudes. Burley and Johnston pointed out that the N(III) compound of NSA may be present as H_2ONO^+ (i.e., protonated HONO). The overall reaction can be written as follows:

$$\mathrm{HONO} + \mathrm{HCl} \Leftrightarrow \mathrm{ClNO} + \mathrm{H_2O} \qquad (1,\text{-}1)$$

The gas-phase enthalpy change for reaction 1 with HONO in the trans form is −4.5 kcal/mol.[8] With a calculated standard entropy change of 3.4 cal mol^{-1} K^{-1},[8] the gas-phase free energy change ($\Delta G°$) at 298 K is approximately −5.5 kcal/mol.

Zhang et al.[9] reported measurements of HONO and HCl reactive uptake in a coated wall flow tube and concluded this reaction could be important in the stratosphere. They found a reaction probability ranging from 0.01 to 0.02 for HCl uptake onto 60−72 wt % sulfuric acid solutions doped with HONO. Although their measurements ($pHCl = pHONO = 3-5 \times 10^{-7}$ Torr) were not done under stratospheric conditions, Zhang et al. estimated that the production of ClNO could be significant, especially under high volcanically perturbed aerosol conditions. In their calculations estimates for HONO solubility were used. However, Becker et al.[10] have recently reported the solubility of HONO in sulfuric acid over wide temperature and composition ranges, which necessitates revising Zhang et al.'s estimates. Using a Knudsen cell, Fenter et al.[11] also studied the reaction of HONO with HCl on sulfuric acid. Interestingly, they observed no reaction between HCl and HONO on solutions containing more than 65 wt % sulfuric acid. At 60 wt % they observed a maximum uptake coefficient for HCl in the presence of HONO of 2×10^{-3}. Because they did not observe ClNO formation at higher wt %, they suggest that NSA is not an important intermediate in this reaction and that this reaction will have a limited impact on the volcanically unperturbed stratosphere.

Because of the discrepancies between the experiments of Zhang et al. and Fenter et al., reinvestigation of this reaction seemed prudent. By measuring the reaction probability (γ), which is composed of fundamental physicochemical parameters,[12] and estimating the heterogeneous processing of this reaction, it should be possible to determine its stratospheric significance. The reaction probability on a sphere of radius a is related to the mass accommodation coefficient (α) and the bulk liquid-phase parameters by the equation:[6]

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{\omega}{4RTH\sqrt{k^{1}D_{l}}f(a/l)} \qquad (2)$$

where ω is the mean thermal speed, H is the Henry's Law coefficient, k^{I} is the first-order loss rate coefficient ($k^{I} = k^{II}H_{HCl}p(HCl)$), D_l is the liquid-phase diffusion coefficient, and l the reacto-diffusive length, $l = (D_l/k^{I})^{1/2}$. $f(a/l)$ represents the

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function [coth(a/l)−l/a] and for bulk measurements or, if $a \gg l$, this factor is equal to unity. From reactive uptake measurements of γ, the quantity $H(k^{\mathrm{I}}D_{\mathrm{l}})^{1/2}$ can be determined and, if H and D_{l} are known or can be estimated, values for k^{I} can be obtained. If eq 2 applies and if all these parameters are known or can be estimated, the reaction probability for reaction 1 can be calculated for application to the atmosphere.[6] In this way, although laboratory measurements of the reaction probability of HONO and HCl are taken under conditions unlike those in the stratosphere, uptake coefficients applicable to the stratosphere can be obtained.

Here we describe experiments on bulk liquids and on aerosol particles that elucidate the reactions of HONO in sulfuric acid solutions. The solubility of HONO in sulfuric acid for a number of different H_2SO_4 concentrations was measured. The reaction of HCl with HONO was investigated on 50, 60, 67, and 70 wt % sulfuric acid solutions. We show that the deviation of the data from bulk phase reaction behavior necessitates including a surface specific term in the equation used to describe the reactive uptake. The hydrolysis of ClNO (-1) on sulfuric acid solutions was also studied to further understand the surface specific behavior. Measurements of HONO and ClNO uptake onto sulfuric acid particles are presented and they indicate the need to consider a surface reaction to describe γ. The reaction of HONO with saturated NaCl solutions was investigated to determine if the presence of protons is necessary for this reaction to take place.

Experimental Section

The uptake in and solubility on bulk liquids was measured in a cylindrical flow tube reactor. The liquid sulfuric acid solutions (50−83 wt % H_2SO_4) were located on the inside wall of the flow tube (i.d. = 2.2 cm)[13] or inside a rotating wetted wall (RWW, i.d. = 1.84 cm) flow reactor, recently developed in our laboratory.[14] For the RWW experiments, the liquid is located on the inside of a glass cylinder that is rotated (0−10 rpm) to maintain a cylindrical coated wall liquid surface. A few experiments were performed with the liquid located in a small container at the bottom of the flow tube.[13]

Solubility Measurements. Because the Henry's Law coefficients for HONO (H_{HONO}) varied over a large range, a few different techniques were employed to measure them. Solubilities were measured using both relative and absolute methods. Solubilities reported here include physical uptake as well as uptake resulting from any further reaction in solution, such as protonation or dissociation, and the values obtained are commonly referred to as effective Henry's Law coefficients.

Relative HONO solubilities were measured by monitoring the partial pressure of HONO over a HONO-doped sulfuric acid solution and varying either the temperature or the water content of the solution. The solutions were prepared by adding HONO from the gas phase to a small amount of solution located in the RWW. HONO was synthesized by adding small amounts of dilute $NaNO_2$ solution to 20 wt % sulfuric acid at 0 °C and transporting the resulting HONO vapor to the flow tube through a movable injector. The solutions in this case were continuously stirred by the slowly rotating RWW and aided by a glass encapsulated stirring bar (~10 cm × 0.5 cm o.d.) that rested in the liquid. The HONO signal (proportional to partial pressure) was then monitored as a function of temperature or of water partial pressure. Care was taken to minimize the amount of HONO desorbed from the solutions during the measurements (i.e., concentration of HONO in the substrate remained constant).

Absolute HONO solubilities were determined in 60 and 65 wt % H_2SO_4 solutions using the RWW flow tube method.[15] Briefly, a known amount of gaseous HONO was absorbed into a known volume of solution (stirred continuously), thus resulting in an absolute measure of the Henry's law coefficient (H_{HONO}). A second type of absolute measurement was performed wherein a nitrosyl−sulfuric acid solution was prepared by adding a known amount of $NaNO_2$ to 80 wt % H_2SO_4 at 0 °C. The composition of this solution was ~0.4 M $NaNO_2$ in ~79 wt % H_2SO_4. The vapor pressure of HONO over these solutions was monitored over a wide temperature range to derive H_{HONO}.

Reactive Uptake Measurements. HONO reactive uptake was studied on 50 (205 and 250 K) and 60 (219, 230, and 250 K) wt % solutions. For the HONO reactive uptake experiments, HCl was introduced into the reactor with the He carrier gas (pHCl, the partial pressure of HCl, was between 10^{-10} and 10^{-7} atm) and allowed to equilibrate with the liquid. Concentration of HCl in the liquid was between $\sim 5 \times 10^{-6}$ and $\sim 3 \times 10^{-2}$ M, dependent on both [H_2SO_4] and temperature (the Henry's law coefficients for HCl were taken from Carslaw et al.[16]). The RWW was primarily used in these experiments. HCl reactive uptake onto 67 (250K) and 71 (215 and 269 K) wt % sulfuric acid solutions that were doped with HONO was studied. HONO was added to the liquid either through the gas phase by including HONO with the carrier gas, feasible when H_{HONO} is relatively low ($<10^5$ M atm^{-1}), or HONO/H_2SO_4/H_2O solutions were prepared by mixing known amounts of $NaNO_2$ with sulfuric acid solutions. ClNO uptake onto 60 wt % sulfuric acid, reaction (-1), was also studied at 250 K. A ~1% mixture of ClNO (99% from Matheson) in He was used. Possible impurities such as Cl_2 or NO in the ClNO were not observed. Even if present these species are not readily taken up by sulfuric acid and would not participate in the observed heterogeneous reaction. For the uptake of HONO on NaCl, a saturated NaCl solution was prepared by placing dry NaCl crystals in the flow tube at 268 K and then adding water vapor to the He flow until the salt appeared wet (deliquesced). The reactive uptake of HONO was then studied.

The average velocity of the He carrier gas (typically 1000 cm s^{-1}) was between 200 and 2000 cm s^{-1}, the total pressure (typically 1 Torr) was between 0.5 and 5 Torr, and the temperature ranged from 205 to 295 K. The standard analysis procedures for flow tubes were used to calculate the reactive uptake coefficients.[17,18] Corrections to the observed first-order rate coefficients due to diffusion ranged from a few percent to as much as 50%. The diffusion coefficients for HONO in He and in H_2O were calculated to be 290 and 75 Torr cm^2 s^{-1} at 220 K, respectively.[19−21]

Gas-phase species (HONO, HCl, and ClNO) were detected using chemical ionization mass spectrometry (CIMS). Within the CIMS, SF_6^- reacts with HCl[22] and HONO (reaction 3a) via flouride transfer. SF_6^- can also transfer a fluorine atom (reaction 3b); the products in this case are ambiguous, but could be HF + NO_2.

$$\mathrm{HONO} + \mathrm{SF_6}^- \rightarrow \mathrm{HF{\cdot}NO_2}^- + \mathrm{SF_5} \qquad (3a)$$

$$\rightarrow \mathrm{SF_5}^- + \text{other products} \qquad (3b)$$

The rate coefficients for reaction 3 have not been reported. Similar to the reaction of SF_6^- with HCl (and unlike the case for SF_6^- + HNO_3), it was found that fluoride ion transfer is not the main channel for reaction of SF_6^- with HONO: primarily SF_5^- is produced. Channel 3b accounts for ~75% of the products, measured by comparing the product ion signals and assuming negligible mass discrimination in the quadrupole mass spectrometer. This differs from the work of Zhang et al.[9] where it was assumed that flouride ion transfer is dominant. They assumed that the rate coefficients for the reactions of HNO_3 and HONO with SF_6^- to give $HFNO_3^-$ and $HFNO_2^-$, respectively, were the same to obtain an estimate for their HONO concentrations; our results show that this is incorrect, as discussed below. Reaction 4 was studied previously by Streit[23] and was reported to have a rate coefficient of 4.4 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 298 K. Our calibrations suggest that this value is too low, see below.

$$ClNO + SF_6^- \rightarrow Cl^- + SF_6 + NO \qquad (4)$$

By monitoring the signal at $HFNO_2^-$, Cl^-, and $HFCl^-$, the reactants and the ClNO product from reaction 1 can be unambiguously identified.

The rate coefficients for reactions 3 and 4 can be estimated (relative to that for HCl + SF_6^-) from the product ion signals where the reaction of ClNO with H_2O, reaction (-1), was observed, and HCl and HONO were assumed to be produced in equal amounts. Because the CIMS signals may depend on the mass of the product ion (i.e., mass discrimination in the instrument) as well as the ion–molecule rate coefficient,[22] the relative rate coefficients are reported as estimates. Note that the CIMS sensitivities for HONO and ClNO, however, are as accurate as for the HCl calibrations, ~25%, subject to the assumption of unity yield for reaction (-1). From the ratio of the product ion signals, a rate coefficient of ~6 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1} is estimated for reaction 3a resulting in an overall rate coefficient for reaction (3a+3b) of ~2 × 10^{-9} cm^3 $molecule^{-1}$ s^{-1}. By comparing the decrease in the Cl^- signal to the increase in the $HFCl^-$ signal, the estimated rate coefficient for (4) is ~2 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}, significantly different than the previously reported value of 4.4 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}.[23] Note also that the rate coefficient we used for the reference reaction of HCl + SF_6^- (1.5 × 10^{-9} cm^3 $molecule^{-1}$ s^{-1} from ref 22) differs substantially from that measured by Streit (4.2 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}).

Using the measured CIMS sensitivity, [HONO] can be estimated:

$$[HONO] = (S_{66}/S_{146})/kt \qquad (5)$$

where (S_{66}/S_{146}) is the ratio of the signals at $HF{\cdot}NO_2^-$ (m/e = 66) and SF_6^- (m/e = 146), k is the rate coefficient for that channel (channel 3a), and t is the average ion molecule reaction time (typically ~5 ms). This estimate is usually accurate to a factor of 2 (+100/−50%), but can be +30/−25% when t is known from calibrations (see below). The initial concentration of HONO in the reactive uptake experiments was in the range of 10^{10} to 10^{11} molecule cm^{-3}. For measuring the gas-phase HONO over the prepared samples of NSA in sulfuric acid and for the HCl reactive uptake measurements, eq 5 was used. For the absolute solubility measurements using the RWW method[15] or the HONO reactive uptake measurements, it is only necessary to know the relative changes in the HONO gas-phase concentrations.

The CIMS was calibrated for HCl by adding a known flow ($\Delta P/\Delta t$ was measured in a known volume) of a dilute HCl mixture to the flow tube. Both a 0.3% HCl-in-He mixture and a 1.0% HCl-in-N_2 mixture were used; the HCl content of the mixtures were known by manometric preparation and were checked by absorption at 185 nm. With the known rate coefficient for SF_6^- + HCl and an analogous equation to eq 5, t can be calculated. It was usually within 30% of the ion molecule reaction time calculated from the CIMS flow tube interaction length (50 cm) and the flow rate (corrected for concentration gradients in a laminar flow[17]).

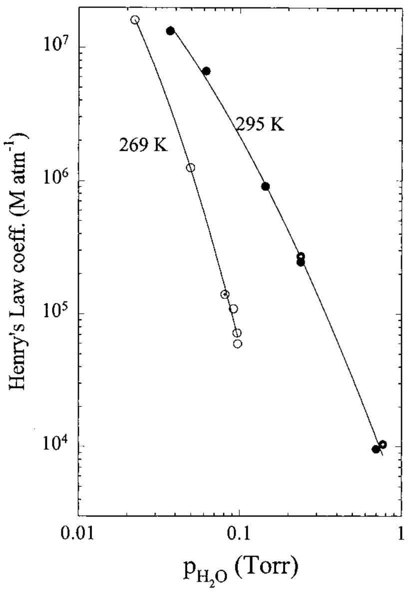

Figure 1. Effective H_{HONO} as a function of water pressure at 269 (open circles) and 295 K (filled circles). The symbols with a cross indicate data taken when the water vapor was increased and agree quite well with data taken when the water vapor was decreased (plain symbols). The lines shown have no physical meaning and are only a visual aid.

Reactions on Aerosol Particles. Reactions 1 and (-1) were also studied on sulfuric acid aerosol particles, primarily at 250 K. HONO and HCl were prepared, delivered, and detected as described above. In separate experiments, ClNO was added to the flow tube via the movable injector from a ~1% mixture in N_2. Sulfuric acid particles were generated by flowing N_2 over hot sulfuric acid after which the particles flowed through a conditioner containing 60 wt % sulfuric acid. The particle number density was measured in an expansion type particle counter. The size distribution was determined from the application of Mie theory to the measured attenuation of UV light scattering by the particles. Detailed experimental descriptions and procedures have been given previously.[24,25]

Results

Relative Henry's Law Coefficients. Shown in Figure 1 are the results of an experiment where the water content of the solutions was changed by varying the partial pressure of water at a constant temperature. Relative H_{HONO} values, which are inversely proportional to the HONO signal and thus partial pressure, were normalized to H_{HONO} determined from absolute measurements (see below). H_{HONO} is strongly dependent on water partial pressure (and thus H_2SO_4 content) of the solutions. In these experiments, the H_2O vapor pressure, calculated from mass flow measurements (see note 23 in Hanson and Lovejoy[15]), was initially 0.1 and 0.7 Torr at 269 and 295 K, respectively. Then the solutions were dried by flowing He over them, a lower H_2O partial pressure was set, and the HONO signal recorded. This process was reversed (i.e., H_2O was added), and the results obtained from drying out and adding H_2O were in excellent agreement. Variations in the volume of the solutions due to changes in density and water content were taken into account when calculating relative Henry's law coefficients. The density of the sulfuric acid solutions was taken from Huthwelker et al.[26] The Henry's law constants determined from these measurements

TABLE 1: Measured Solubility Values

T, K	acid, wt %	Henry's law coeff, M atm^{-1}	method	uncertainty
295	83	1.3×10^7	relative	+100/− 50%
295	82	6.6×10^6	relative	+100/− 50%
295	79	9.1×10^5	relative	+100/− 50%
295	79	1.5×10^6	abs. molarity[a]	+150/−65%
292	79	3.1×10^6	abs. molarity	+150/−65%
280	79	8.5×10^6	abs. molarity	+150/−65%
274	79	1.6×10^7	abs. molarity	+150/−65%
273	79	1.6×10^7	abs. molarity	+150/−65%
261	79	7.7×10^7	abs. molarity	+150/−65%
250	79	2.8×10^8	abs. molarity	+150/−65%
230	79	4.6×10^9	abs. molarity	+150/−65%
269	77	1.7×10^7	relative	+100/− 50%
295	76.5	2.6×10^5	relative	+100/− 50%
269	74	1.3×10^6	relative	+100/− 50%
269	72	1.4×10^5	relative	+100/− 50%
295	71	9.8×10^3	relative	+100/− 50%
271	71	9.3×10^4	relative	+100/− 50%
269	71	9.1×10^4	relative	+100/− 50%
249	71	1.1×10^6	relative	+100/− 50%
230	71	1.2×10^7	relative	+100/− 50%
269	70.5	5.9×10^4	relative	+100/− 50%
295	70	6.3×10^3	abs. RWW	+30/−25%
270	70	5.8×10^4	abs. RWW	+30/−25%
296	66	1.2×10^3	abs. RWW	+30/−25%
270	66	4.2×10^3	abs. RWW	+30/−25%
270	65	2.6×10^3	abs. RWW	+30/−25%
249	65	9.0×10^3	abs. RWW	+30/−25%
240	65	2.4×10^4	abs. RWW	+30/−25%
220	65	1.6×10^5	abs. RWW	+30/−25%
240	60	3.0×10^3	abs. RWW	+30/−25%
220	60	2.7×10^4	abs. RWW	+30/−25%
218	60	4.1×10^4	abs. RWW	+30/−25%

[a] abs. molarity = absolute molarity.

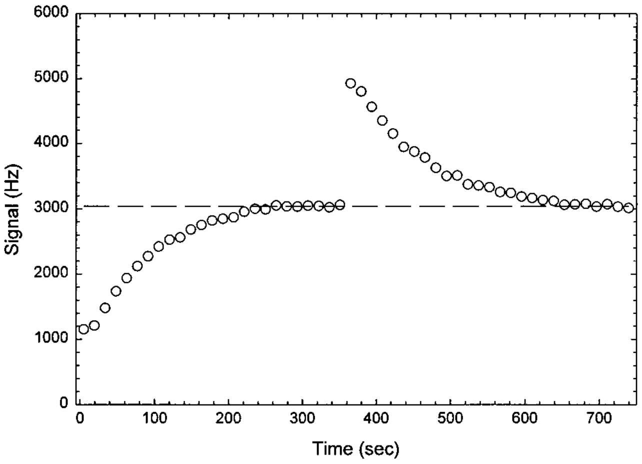

Figure 2. HONO gas-phase signal measured by the CIMS as a function of time. By monitoring the absorption or desorption of HONO into a known amount of sulfuric acid an absolute solubility can be measured.

after normalization are given in Table 1 (relative measurements).

Absolute Henry's Law Coefficients. The physical uptake of HONO onto 60 and 65 wt % H_2SO_4 solutions was investigated over a range of temperatures (218−273 K). Data for the uptake/solvation of HONO into ~0.44 cm^3 of 65 wt % H_2SO_4 at 249.5 K are shown in Figure 2. Both the uptake and desorption of HONO are shown and the amount of HONO absorbed is equal to that which is desorbed (within 10%). Results for a number of such experiments are presented in Table 1 (absolute RWW measurements).

Shown in Figure 3 are the measured partial pressures of HONO over the 0.4 M HONO in 79 wt % H_2SO_4 solution as a function of 1/T. The solution temperature was varied from 295 K down to 230 K and then back to 296 K with good reproducibility in the vapor pressure of HONO. H_{HONO} in 79 wt % H_2SO_4 can be obtained from these data and these values are given in Table 1 (absolute molarity measurements). A small correction to the [HONO] in solution from the increase in solution density as the temperature drops (~5% from 295 to 230 K) was applied.

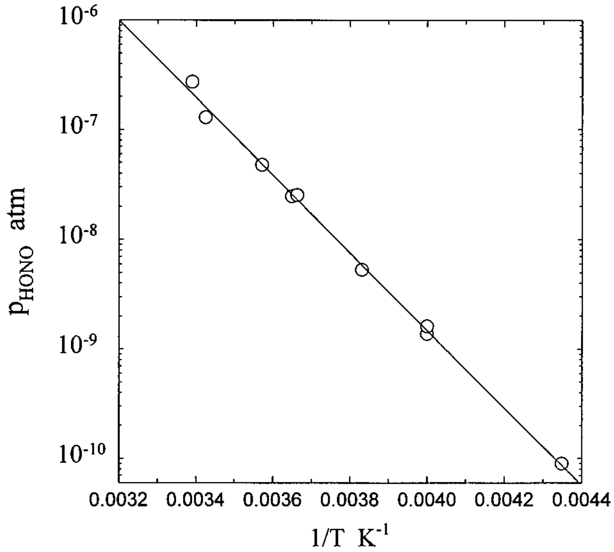

Figure 3. A second type of absolute Henry's law measurement in which the HONO concentration in solution is known and the HONO pressure is monitored as a function of temperature. The HONO concentration is ~0.4 M in 79 wt % sulfuric acid.

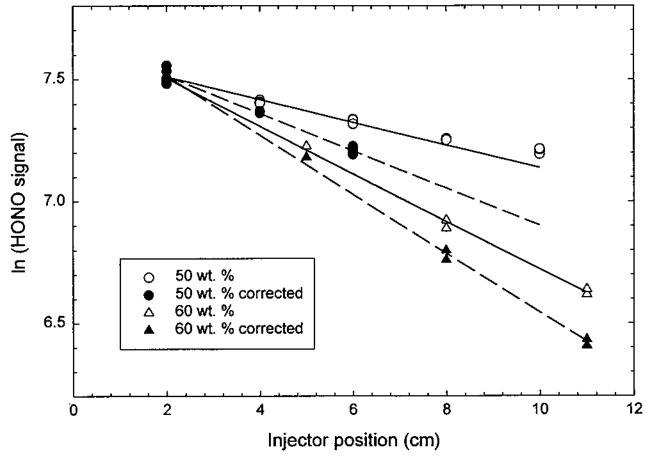

Figure 4. Plot of the raw data (open symbols) from the loss of HONO on 50 and 60 wt % sulfuric acid solutions with HCl at 250 K. The solid lines are a linear fit through the data up to an injector position of 6 (11 for 60 wt %) cm. The effects of equilibrium become quite pronounced at injector positions greater than 6 for the 50 wt % data. The data points are corrected for the production of HONO from ClNO (solid symbols) for both 50 and 60 wt %. The dashed lines are the fit through the corrected data and γ was calculated from these corrected slopes. See text for details.

Reactive Uptake of HONO on HCl-Doped Solutions. The reaction probabilities for HONO were measured over a range of HCl partial pressures. No reaction between HONO and HCl was observed without sulfuric acid present (i.e., no reaction in the gas phase or on glass). Figure 4 shows the data for HONO uptake on 50 and 60 wt % sulfuric acid at 250 K. As the reaction is monitored over longer contact times, the observed loss of HONO (at 50 wt % especially) slows for injector positions larger than ~6 cm. The reaction begins to reach equilibrium (i.e., [ClNO][H_2O]/[HCl][HONO] approaches K_{eq}

$= \exp(-\Delta G°/RT)$) and the hydrolysis of ClNO results in significant production of HONO. The effect at 50 wt % sulfuric acid is thought to be more pronounced because of higher [H_2O], which increases the rate of the reaction in the reverse direction.

To account for this equilibrium effect as fully as possible, the raw data points were corrected for the amount of HONO produced from the reaction of ClNO with H_2O. This was done by taking into account the amount of HONO produced from ClNO at each injector position, the uptake coefficient for ClNO (based on experiments discussed below), and the average reaction time (injector position/average flow velocity.) In addition, the fraction of this HONO produced that reacted with HCl was calculated.[27] As illustrated in Figure 4, this correction can be significant. The data shown is typical for the 50 wt % measurements, and without correcting for HONO production from ClNO γ would by underestimated by ~40%. Most measurements did not require such a large correction; for example, the uncorrected 60 wt % data would yield a 20% lower γ on average. Neither Zhang et al.[9] or Fenter et al.[11] reported the occurrence of the reverse reaction in their experiments. We found that the effects of reverse reaction (-1) could be obscured if the reaction was not taking place under pseudo-first-order conditions in HONO (i.e., [HCl] in solution was not at least 6 times greater than the [HONO]).

The dependence of γ on HCl pressure for 50 wt % sulfuric acid solutions at 205 and 250 K is illustrated by a log(γ)−log(pHCl) plot (Figure 5a). The slope of the linear fit to the 50 wt % data at 205 K is 0.53 ± 0.08. The uncertainty here, as well as in all the log(γ)−log(pHCl) measurements, represents 2σ in the fit. γ_{HONO} was weighted in the fits by uncertainties of one-half the difference between the uncorrected value and the value corrected for HONO production from ClNO (averaged ± 12% for the 50 wt % data at 205 K). The value of 0.53 is close to the value of 0.5 expected from eq 2 indicating that HONO uptake can be described using a bulk reaction with HCl at 205 K. However, at 250 K the slope is 0.80 ± 0.22, indicating that the reaction of HONO with HCl cannot be completely described as a bulk reaction (γ uncertainties averaged ±38%). Alternatively, the same data can be plotted as Γ versus $(\mathrm{pHCl})^{1/2}$ where $1/\Gamma = 1/\gamma - 1/\alpha$. The data plotted in this manner should lie on a straight line if the reaction probability can be described by bulk processes and the mass accommodation coefficient is ~1.

$$\Gamma = \frac{4RTH_{\mathrm{HONO}}\sqrt{k^{\mathrm{II}}H_{\mathrm{HCl}}(\mathrm{pHCl})D_l}}{\omega} \qquad (6)$$

As expected, a linear fit of Γ vs $(\mathrm{pHCl})^{1/2}$ represents the 205 K data reasonably well (Figure 5b), but does not describe the 250 K data as depicted in Figure 5c. Since γ for HONO is not linearly dependent on $(\mathrm{pHCl})^{1/2}$ in 250 K sulfuric acid, the reaction of HONO with HCl likely has a contribution resulting from a surface specific reaction on sulfuric acid. In these experiments, $\alpha \gg \gamma$ and the curved behavior cannot be attributed to $\gamma \rightarrow \alpha$. In addition, varying α from 0.1 to 1 does not effect this behavior.

A surface reaction term, which is proportional to the HCl content of the liquid (H_{HCl}(pHCl)), can be added to eq 6.[28,29]

$$\Gamma = \frac{4RTH_{\mathrm{HONO}}\sqrt{k^{\mathrm{II}}H_{\mathrm{HCl}}(\mathrm{pHCl})D_l}}{\omega} + k_{\mathrm{sur}}H_{\mathrm{HCl}}(\mathrm{pHCl}) \qquad (7)$$

$$\Gamma = a_1\sqrt{\mathrm{pHCl}} + a_2(\mathrm{pHCl}) \qquad (8)$$

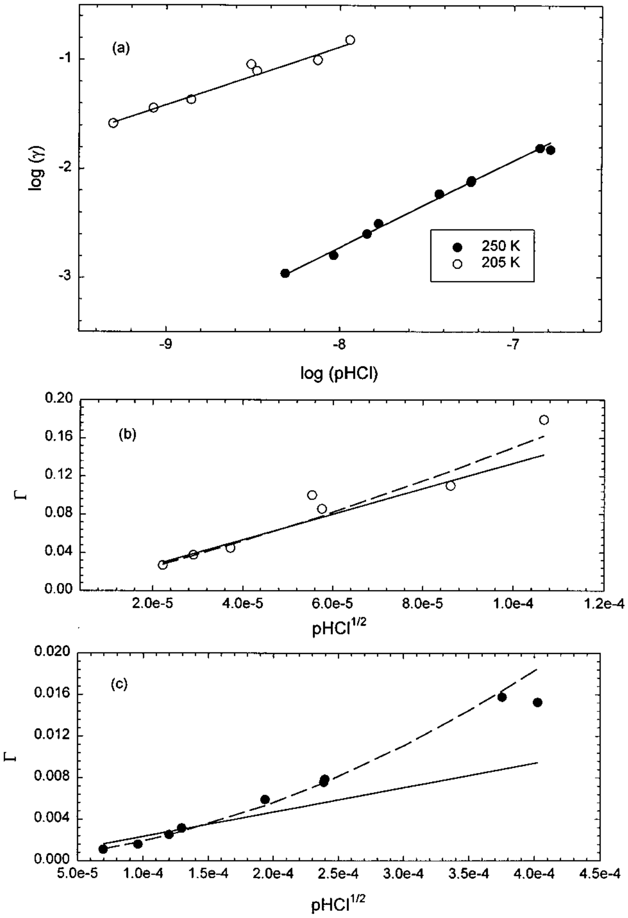

Figure 5. Data taken at 50 wt % and 205 and 250 K. (a) Log(γ)−log(pHCl) plot illustrating the relationship between HCl pressure and the uptake coefficient. (b) The fit to the data at 205 K using eq 2 (solid line) is nearly identical to that from eq 8 (dashed line). (c) It becomes clear in this plot that eq 2 is not adequate to completely explain the reaction taking place at 250 K. By including a surface contribution (dashed line) the data is reproduced significantly better.

Equation 7 (and thus 8) is an approximation[29] which, for the results presented here (i.e., $\gamma \leq 0.1$), can be considered a good one. The dashed line in Figure 5b is a second-order fit to γ versus $(\mathrm{pHCl})^{1/2}$ according to eq 7. Values for a_1 and a_2 (eq 8) are given in Table 2 for all the measurements where a_1 is related to the liquid-phase second-order rate coefficient (k^{II}) and a_2 is related to a surface specific reaction rate coefficient (k_{sur} M^{-1}). Values for k^{II} were obtained by calculating H_{HCl}[16] and using the H_{HONO} measured in this work or, for 50 wt %, that of Becker et al.[10] D_l for HONO was calculated by assuming the same parameters that were used for HOCl.[26]

At 60 wt % it was necessary to use only measurements wherein the HCl concentration in the solution phase was at least a factor of 6 higher than the HONO concentration. This is because H_{HONO} is larger than H_{HCl} at 60 wt % and higher [HCl] than [HONO] in the liquid phase is necessary to ensure first-order conditions in HONO. Figure 6 consists of (a) a log(γ)-log(pHCl) plot and (b) a Γ vs $\mathrm{pHCl}^{1/2}$ plot, comparing the data at 219, 230, and 250 K. The results and parameters used for both 50 and 60 wt % are also compiled in Table 2. The 2σ uncertainties in the fits to a_1, and therefore in k^{II}, are given in Table 2 and average ±56%. This does not represent the total uncertainty in calculating k^{II} as uncertainties in H_{HCl}, H_{HONO}, and D_l are not included. Most of the measurements exhibit surface specific behavior except at 60 wt %, 219 K and 50 wt %, 205 K where the reaction occurs primarily in the bulk.

TABLE 2: Uptake Measurements

T, K	acid, wt %	log−log slope ± 2σ	H_{HONO}, M atm^{-1}	H_{HCl}, M atm^{-1}	D_{l}, cm^2 s^{-1}	k^{II}, M^{-1} s^{-1}	$a_1 \pm 2\sigma$	a_2
				HONO Uptake				
250	50	0.80 ± 0.22	3.0×10^2	2.5×10^4	9.5×10^{-7}	8.1×10^3	10 ± 11	8.9×10^4
205	50	0.53 ± 0.08	4.2×10^4	3.0×10^6	3.6×10^{-8}	1.5×10^3	1200 ± 250	3.3×10^6
250	60	0.78 ± 0.10	1.3×10^3	8.6×10^2	6.3×10^{-7}	9.4×10^4	23 ± 11	1.9×10^5
230	60	0.66 ± 0.06	1.0×10^4	4.7×10^3	1.9×10^{-7}	6.9×10^4	180 ± 38	8.3×10^5
219	60	0.47 ± 0.16	4.0×10^4	1.4×10^4	7.1×10^{-8}	5.0×10^4	640 ± 530	0
				HCl Uptake				
269	70	0.92 ± 0.24	1.5×10^5	5.7	9.6×10^{-7}	5.8×10^4	1.2 ± 3.9	8.7×10^4
215	70	0.46 ± 0.10	1.0×10^8	2.3×10^2	1.7×10^{-8}	3.5×10^5	350 ± 25	0
250	67	0.90 ± 0.18	$\sim 7 \times 10^4$	60	8.0×10^{-7}	3.9×10^4	6.9 ± 11	3.8×10^5

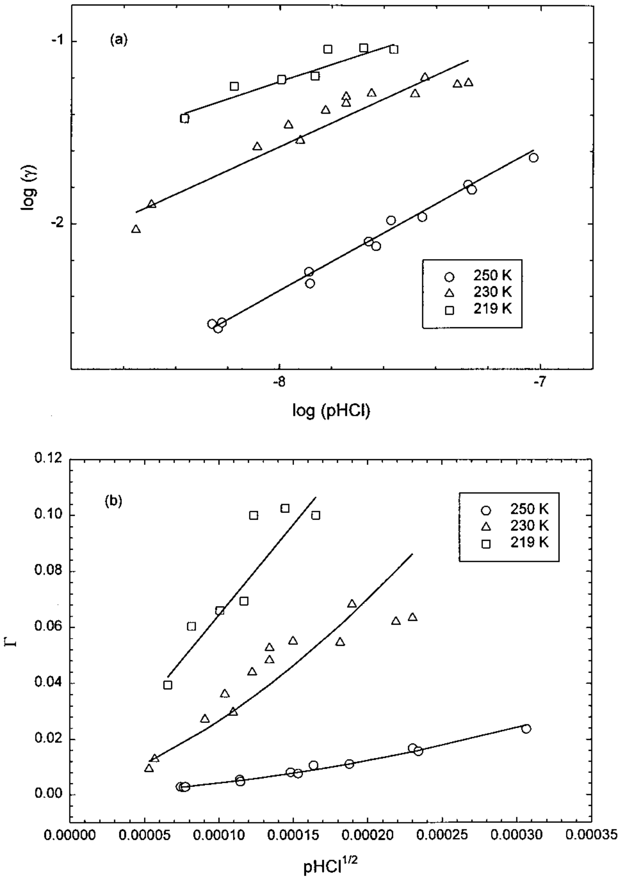

Figure 6. Data from 60 wt % solutions at 219, 230, and 250 K are compared. Figure 6a is similar to Figure 5a. The solid lines in Figure 6b are fits using eq 8 and assuming a surface specific reaction.

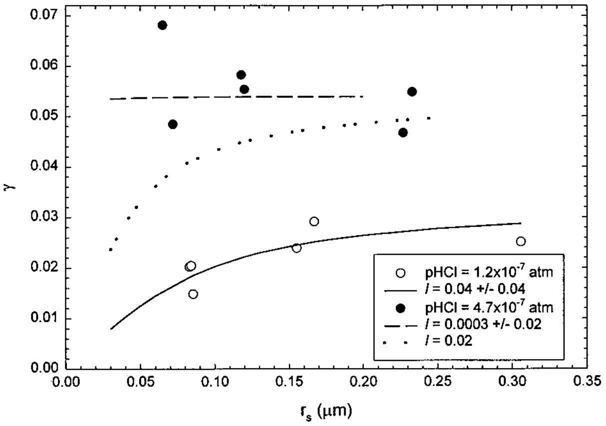

Figure 7. A plot of measured reactive uptake coefficients versus particle size at 250 K, 60 wt %, and two HCl pressures. The solid line is a fit of the data to eq 9 at 1.2×10^{-7} atm allowing both l and Γ to vary. For the high-pressure data the short dashed line indicates the fit while the upper limit to l is also plotted (dotted line).

Reaction of HONO on HCl-Doped Sulfuric Acid Aerosol. The reactive uptake of HONO onto HCl-doped 60 wt % sulfuric acid aerosol particles was studied as a function of particle size at 250 K. The production of HONO from the reverse reaction (-1) was taken into account, as in the bulk reactions. In Figure 7 the measured γ from the aerosol experiments is plotted against r_s, the surface-area weighted particle radius.[14] r_s is a good approximation (for log-normal distributions with geometric standard deviations ≤1.26)[14] that takes into account the polydisperse aerosol samples that we use. No significant size dependence for γ was observed in the pHCl range from 1 to 5 × 10^{-7} atm. The lines are fits to the data according to eq 2, which rearranges to eq 9. Γ, defined by either eq 6 or eq 7

$$\gamma = \frac{\alpha\Gamma f(r_s/l)}{\alpha + \Gamma f(r_s/l)} \cong [\coth(r_s/l) - l/r_s]\Gamma \qquad (9)$$

depending on whether a surface contribution is present, is treated here as variable to be fit, as is l. Here we assume no surface contribution to illustrate that the measured γ on particles can be directly related to the reacto-diffusive length.

From the second-order rate coefficient (k^{11}) that was obtained from the 60 wt % bulk data at 250 K, a reacto-diffusive length of 2.6 μm is predicted for an HCl pressure of 1 × 10^{-7} atm. However, as evident in Figure 7, a reacto-diffusive length of 0.04 ± 0.04 (±2σ) μm can represent the data. A similar trend is also observed at higher HCl pressures where an l value of 1.3 μm is predicted, yet the data indicates an l value of essentially zero (l < 0.02). Since the reacto-diffusive length can be considered a measure of the depth over which the reaction is taking place, this small value is an indication that a surface reaction is dominating the conversion. Note that these measurements do not yield a value for l for the bulk phase reaction; rather they should be considered further evidence that this reaction has a surface component.

Reactive Uptake of HCl on HONO-Doped Solutions. HCl loss measurements onto ~70 wt % sulfuric acid solutions doped with HONO were measured at 215 and 269 K. Reactive uptake measurements on 67 wt % solutions at 250 K were also carried out. It was necessary to dope the solutions with HONO and follow the HCl uptake as the large H_{HONO} for these sulfuric acid compositions ($H_{\mathrm{HONO}} \gg H_{\mathrm{HCl}}$) precludes pseudo-first-order conditions for HONO in the liquid. These data was not corrected for HCl production from reaction (-1) as the quantity [ClNO][H2O]/[HONO][HCl] was far from the equilibrium value ($K_{\mathrm{eq}} = \exp(-\Delta G°/RT)$). Uncertainties in γ averaged ±15%.

Figure 8a is a log(γ)−log(pHONO) plot for three different conditions. At 250 and 269 K the slope is close to 1 (0.90 ± 0.18 and 0.92 ± 0.24, respectively), while at 215 K and 70 wt

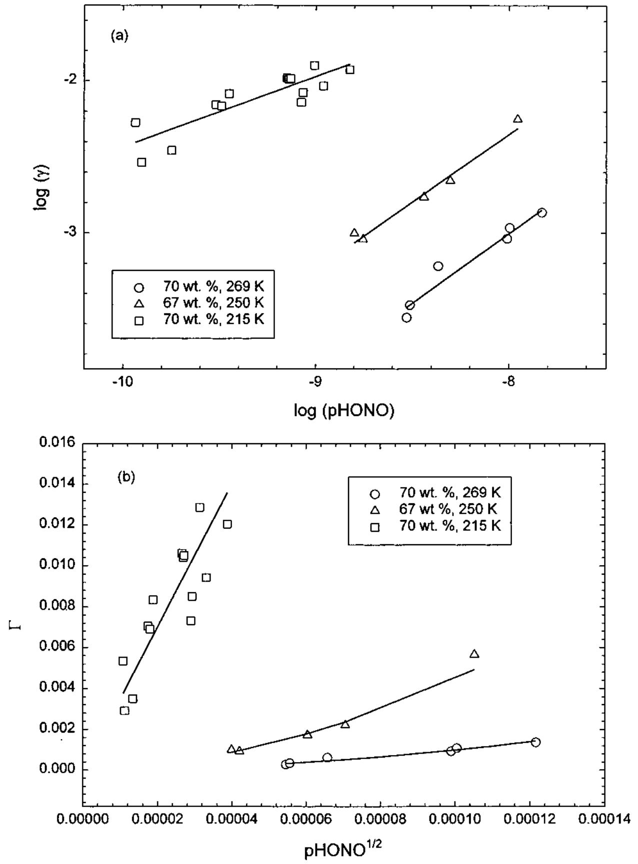

Figure 8. (a) Log(γ)$-$log(pHONO) plots of 70 and 67 wt % data at 215, 269, and 250 K. (b) A plot of Γ versus p(HONO)$^{1/2}$ allows k^{II} to be extracted.

% the data can be fit with a slope of 0.46 ± 0.10. Figure 8b is a plot of Γ(HCl) versus (pHONO)$^{1/2}$ for these different conditions. Similar to the HONO uptake experiments, a second-order rate coefficient (k^{II}) can be extracted and these values are listed in Table 2. D_{l} for HCl was calculated analogously to that for HONO with slight modifications for HCl.[30] The large uncertainty in a_{l} (Table 2) at 269 K reflects the fact that these data could be fit without a contribution from the bulk reaction. This uncertainty is also reflected in the k^{II} values. Not included are uncertainties due to the Henry's law coefficients and D_{l} as discussed earlier.

Reverse Reaction: ClNO Hydrolysis. The reaction probability for loss of ClNO due to hydrolysis (-1) was investigated at 250 K on 50 and 60 wt % sulfuric acid in the RWW. A small correction for the effect of reaction 1 on the observed ClNO loss rate coefficient was made. There was no evidence of impurities in the ClNO affecting the uptake. The average reaction probability for ClNO was $(2.5 \pm 0.8) \times 10^{-3}$ on 60 wt % and $(3 \pm 1) \times 10^{-3}$ on 50 wt % H_2SO_4 at 250 K. Without making assumptions about ClNO solubility, which would be unreliable, or postulating that no surface-specific reaction is occurring, which would be incorrect, it is not possible to determine the bulk hydrolysis rate coefficients for ClNO.

The reaction probability for loss of ClNO due to hydrolysis was also investigated as a function of particle size at 250 and 294 K on 60 wt % sulfuric acid aerosol particles. These results are plotted in Figure 9 and no significant dependence on size was found ($l \leq 0.02$ μm at both temperatures). The reaction probability at 250 K is in good agreement ($\gamma = 2.5 \times 10^{-3}$) with that measured over bulk solutions here. The average γ measured on particles at 294 K, 5.0×10^{-3}, indicates that γ_{ClNO} is temperature dependent.

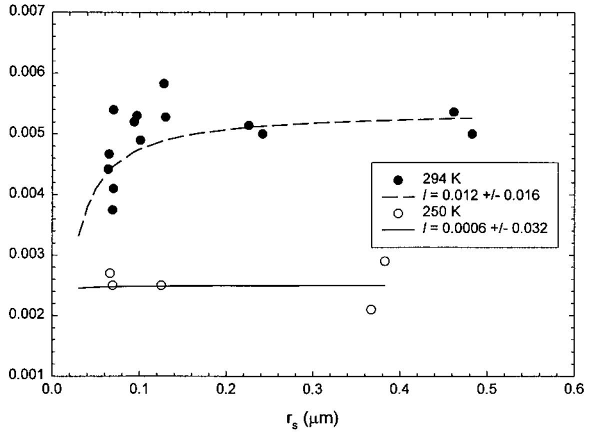

Figure 9. ClNO uptake onto 60 wt % sulfuric acid aerosols at 250 and 294 K as a function of the surface area weighted particle radius. This reaction also shows the effect of a surface reaction with small l values necessary to fit the data.

HONO Uptake onto NaCl Solutions. No reaction of HONO with Cl^- to give ClNO was observed over saturated NaCl solutions (~6 M) at 268 K. The signal due to ClNO showed no increase; however, in some experiments, production of HONO was noticed. HONO is not produced exclusively in the source. NO_2, NO, and H_2O are in equilibrium with HONO as shown in reaction 10.[31]

$$\mathrm{2HONO \leftrightarrow H_2O + NO + NO_2} \qquad (10,-10)$$

Either reaction (−10) or reaction 11 could lead to HONO production if [H_2O] is significantly different in the flow tube than in the HONO source.

$$\mathrm{2NO_2 + H_2O \rightarrow HONO + HNO_3} \qquad (11)$$

The high [H_2O] in the flow tube, which was necessary to saturate the NaCl, probably led to the HONO production. In the experiments over sulfuric acid, the water vapor pressure was much lower and production of HONO was not observed. These experiments over saturated NaCl solutions indicate that the reaction of HONO with Cl^- requires the presence of protons to be efficient.

Discussion

HONO Solubility. The solubility of HONO in H_2SO_4 solutions is a strong function of acid content. As found by Becker et al.,[10] HONO is much more soluble in strong acid (~60−70 wt % H_2SO_4) than in more dilute H_2SO_4 (~50 wt %). Plotted in Figure 10 is the Henry's law coefficient (M atm^{-1}) versus H_2SO_4 content for 295 K (open symbols) and 269 K (filled symbols) (both relative and absolute). The H_2SO_4 content was calculated from the water partial pressure and temperature for the data presented in Figure 1.[32] To apply all the data in Table 1 to this figure, some of the data was "corrected" for a small temperature difference ($\Delta T < 3$ K) using a $\Delta H^\circ_{\mathrm{sol}}$ of −15 kcal mol^{-1}. Also shown as the triangles are the data of Becker et al.[10] corrected for [HONO] reported in mol kg^{-1} solution^{-1} to mol L^{-1} (small T corrections were also made to some of these data). There is excellent agreement between the results of the present work and the results of Becker et al. Our results extend the range over which H_{HONO} has been measured to 79 wt % H_2SO_4 and to temperatures as low as 220 K.

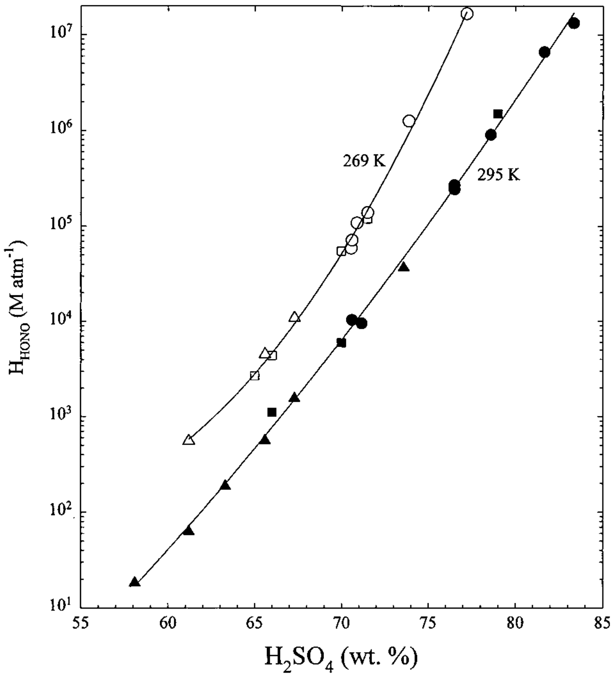

Figure 10. Effective H_{HONO} values as a function of sulfuric acid wt % at 269 (open symbols) and 295 K (filled symbols). The circles represent relative measurements from this work, while the squares are absolute measurements from this work. The triangles are measurements from Becker et al.

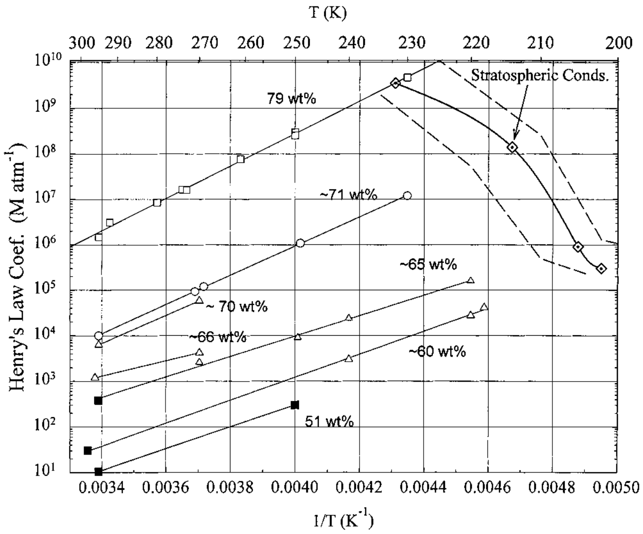

Figure 11. Plot of effective Henry's law constants as function of 1/*T*. The open squares are absolute measurements at 79 wt %, analogous to Figure 3. The open circles are relative measurements while the RWW absolute measurements are represented by open triangles. The filled squares are from Becker et al.'s measurements.[10] Extrapolating to stratospheric conditions ($pH_2O = 2 \times 10^{-4}$ Torr), H_{HONO} is 3×10^5 M atm^{-1} in 60 wt % acid at 202 K increasing to 9×10^5, 1×10^8, and 4×10^9 M atm^{-1} in 65, 71, and 79 wt % (205, 215, 232 K, respectively). The dashed lines on either side of the diamond symbols, which represent stratospheric conditions, illustrate the variation of H_{HONO} as the water vapor pressure varies from 1×10^{-4} to 4×10^{-4} Torr.

Figure 11 is a master plot of the measured HONO solubilities reported here vs 1/*T* for several H_2SO_4 solutions. Also included are some of the results of Becker et al.[10] A plot of ln(*H*) vs 1/*T* results in values of $\Delta H°_{sol}$ for HONO.[33] $\Delta H°_{sol}$ for HONO in 79 wt % H_2SO_4 is −16 kcal mol^{-1}, that for ~71 wt % is −15 kcal mol^{-1}, at 65 wt % it is −10 kcal mol^{-1}, and in 60 wt % H_2SO_4 $\Delta H°_{sol}$ is −11.5 kcal mol^{-1}. These are effective solvation enthalpies and include solvation as well as protonation, dissociation, or association. The difference in ΔH_{sol} at 60 and 65 wt % as compared to 71 and 79 wt % most likely indicates a change in the form of HONO in solution. Becker et al. observed a dramatic change in the variation of H_{HONO} with H_2SO_4 content near 53 wt %, which they attributed to the formation of NO^+ via the equilibrium reaction 12.

$$HONO + H^+ \leftrightarrow H_2O + NO^+ \tag{12}$$

However, there are other possibilities, such as H_2ONO^+, which has also been identified by spectroscopic techniques in solution.[7] From the strong evidence of a species shift at 53 wt % in Becker et al.'s work, we agree that the form of N(III) in solution is HONO below 53 wt %. However, from our effective solvation values we suspect that the equilibrium is more complicated than as represented by eq 12. It is possible that primarily H_2ONO^+ is the N(III) species in 60 and 65 wt %, and a mixture of H_2ONO^+ and $NO^+HSO_4^-$ is present in 71 and 79 wt % solutions.[34]

Atmospheric Implications. The amount of N(III) (i.e., HONO, H_2ONO^+, and $NO^+HSO_4^-$) found in stratospheric aerosols can be estimated from the results of this work assuming HONO is in gas−liquid equilibrium. Here we use a gas-phase HONO concentration of 1×10^7 molecule cm^{-3}, a relatively high estimate for the unpolluted stratosphere;[35] this is equivalent to a HONO partial pressure of $\sim 3 \times 10^{-13}$ atm. The concentration of N(III) in 79 wt % sulfuric acid at 232 K would be $\sim 1.2 \times 10^{-3}$ M using our measured Henry's law constant. At 71 wt % and 215 K a sulfuric acid aerosol would contain $\sim 3 \times 10^{-5}$ M N(III), and in a 60 wt % aerosol at 202 K the concentration would be $\sim 9 \times 10^{-8}$ M. Even at high HONO concentrations, as measured in airplane plumes (0.52 ppbv $\sim 2 \times 10^9$ molecule cm^{-3}),[35] the concentration of N(III) in solution would be 0.23 M, 5.9×10^{-3}, and 1.8×10^{-5} at 79, 71, and 60 wt %, respectively. Burley and Johnston calculated that N(III) could be as high as 1% of the sulfuric acid solution or ~0.15 M in a 60 wt % aerosol; this could not result from HONO uptake unless HONO was on the order of 5 ppmv.

To extrapolate our measured γ values to the stratosphere it is necessary to know k^{II}, H_{HONO}, H_{HCl}, and D_l. Assuming an HCl concentration of 2×10^9 molecule/cm^3, a γ_{strat} for HONO uptake can be calculated using the following eq 13, which differs

$$\Gamma_{calc} \equiv \frac{4H_{HONO}RT\sqrt{k^I D_l}}{\omega} f(r_s/l) + k_{sur}H_{HCl}(pHCl) \tag{13}$$

from eq 7 only by including the $f(r_s/l)$ term.

l is equal to$(D_l/k^I)^{1/2}$ and r_s is taken to be 0.1 μm to represent background sulfuric acid aerosol conditions. To estimate Γ_{calc}, the reaction rate parameters were taken to be the values measured here at the lowest temperatures. The diffusion coefficients for HONO and for HCl were calculated as in Huthwelker et al.[26] and Luo et al.[30] The H_{HONO} were taken from extrapolations of the measured H_{HONO} (present work and Becker et al.[10]) and H_{HCl} were taken from the calculations of Carslaw et al.[16] These parameters and the resulting Γ_{calc} are shown in Table 3. Note that Γ_{calc} differs from γ by less that 0.2%.

The processing of HCl from reaction with HONO can be estimated from the loss of HONO in the stratosphere via eq 14[36]

TABLE 3: Calculated Reaction Probabilities for HONO + HCl at Stratospheric Conditions

T, K	acid, wt %	k^{II}, M^{-1} s^{-1}	k_{sur}, M^{-1}	D_l, cm^2 s^{-1}	H_{HONO}, M atm^{-1}	H_{HCl}, M atm^{-1}	Γ^a
195	50	1.5×10^3	1.1	9.2×10^{-9}	1.8×10^5	1.0×10^7	1.6×10^{-3}
205	60	5.0×10^4	0	1.6×10^{-8}	3×10^5	4.8×10^4	3.0×10^{-4}
215	70	3.5×10^5	0	1.7×10^{-8}	1.0×10^8	2.3×10^2	$1.5 \times 10^{-5\,b}$

[a] Reaction probability for HONO assuming [HCl] = 2×10^9 molecule cm^{-3} and $r_s = 0.1$ μm. [b] Reaction probability for HCl assuming [HONO] = 1×10^7 molecule cm^{-3} and $r_s = 0.1$ μm.

$$-\frac{\mathrm{dHCl}}{\mathrm{d}t} = -\frac{\mathrm{dHONO}}{\mathrm{d}t} = \frac{\gamma\sigma_A\omega[\mathrm{HONO}]_{\mathrm{strat}}}{4} \qquad (14)$$

where σ_A is the aerosol surface area per unit volume, $\sigma_A = 2 \times 10^{-8}$$cm^{-1}$ is typical for nonvolcanic conditions, and $[HONO]_{strat}$ is 1×10^7mol cm^{-3}. The processing of HCl at 60 wt % and 205 K is 0.4 molecule cm^{-3} s^{-1}, while at 50 wt % and 195 K it is 1.5 molecule cm^{-3} s^{-1}. At 70 wt % and 215 K (replace $[HONO]_{strat}$ with $[HCl]_{strat} = 2 \times 10^9$ molecule/cm^3 and replace Γ_{HONO} with $\Gamma_{HCl} = 1.5 \times 10^{-5}$), the HCl processing rate is 5.3 molecule cm^{-3} s^{-1}. The major loss process for HCl in the stratosphere at these warmer temperatures (i.e., >210 K) is reaction with OH (typically 1×10^6 molecule cm^{-3} s^{-1}), which results in a processing rate for HCl of ~1200 molecule cm^3 s^{-1} for these conditions.[37] These calculations indicate that reaction with HONO (even at a relatively high concentration of 1×10^7 mol cm^{-3}) is not a significant loss process for HCl.

Our results differ from Fenter et al.[11] in that we do observe reaction of HONO and HCl in sulfuric acid solutions greater than 65 wt % acid. The high values for γ observed by Zhang et al.[9] (0.01−0.02 for 60−72 wt %) were not measured under stratospheric conditions; their reactant concentrations of 3−5 × 10^{-7} Torr (~1×10^{10} molecule/cm^3 at 215 K) are higher than what would be found in the stratosphere, especially for HONO. If γ is calculated for their conditions, similar to the process used in Table 3, a value of ~5×10^{-3} is obtained at 220 K for 70 wt % solutions; this differs somewhat from their measurement of 1.9×10^{-2}. Their ClNO production rate of 34 molecule cm^{-3} s^{-1} ($\sigma_A = 6 \times 10^{-9}$ cm^{-1}) at 70 wt % under nonvolcanic conditions is significantly higher than our estimate for this σ_A (1.6 molecule cm^{-3} s^{-1}), which may be due to their overestimation of γ.

Under volcanic conditions (for example, a log-normal distribution with $r_p = 0.35$ μm, log $\sigma = 0.2$, and total number density = 35 particles cm^{-3}; results in $\sigma_A = 8.4 \times 10^{-7}$ cm^{-1}),[38] we estimate a ClNO formation rate of ~1500 molecule cm^{-3} s^{-1}. Zhang et al. estimated ~5000 molecule cm^{-3} s^{-1} for comparable σ_A; however, their estimation procedure did not take into account any size dependence to γ. For d[HCl]/dt = 1500 molecule cm^{-3} s^{-1}, HCl processing by sulfuric acid particles is comparable to that of reaction with OH. Note that this estimate is based on a highly perturbed sulfuric acid aerosol layer and a relatively high [HONO] of 1×10^7 molecule cm^{-3}. We should reiterate here that it is necessary to calculate γ under stratospheric conditions before making estimates about production rates. Zhang et al. assumed $\gamma_{HONO} = 0.07$, which is not applicable for the reaction occurring in 70 wt % acid solutions at stratospheric conditions.

Surface Reaction. Evidence for the reaction of HONO with HCl occurring on the surface is: (i) γ_{HONO} is not proportional to $(pHCl)^{1/2}$ for many experiments and (ii) γ_{HONO} on HCl-doped sulfuric acid aerosol has little or no dependence on particle size ($l \leq 0.04$ μm). Hanson and Ravishankara,[28] Hu et al.,[39a] and Jayne et al.[39b,c] have previously identified surface contributions in heterogeneous reactions. These observations are typically based on the inability of equations derived using bulk phase assumptions to explain the data (i.e., point (i) above). In our experiments the aerosol data adds a second piece of evidence that there is a surface component to this reaction. Furthermore, we do see a variation in the importance of the surface reaction with temperature and sulfuric acid wt %. k_{sur} (a_2/H_{HCl} for 50 and 60 wt %, a_2/H_{HONO} for 70 wt %) is expressed most at high temperatures and in 60 wt % H_2SO_4, we do not know why the surface reaction would be favored under these conditions.

There is additional evidence for the surface reaction in that the γ_{ClNO} on aerosols is independent of particle size down to 0.05 μm ($l < 0.02$ μm). This indicates that the reverse reaction (-1) is also facilitated at the surface. It is possible that the fractional HCl content on the surface could be high and cause what appears to be a surface-specific effect for reaction 1 (l could be small because of high HCl). In this case, the reverse reaction of ClNO + H_2O would not show the surface effect. Because ClNO hydrolysis is probably enhanced at the surface, it is likely that the surface reaction term for reaction 1 is due to the special environment of the surface rather than only an enhancement of one or both of the reactant concentrations at the surface.

Our measurements indicate that k^{II} can be higher (see Table 2) than the rate suggested by Burley and Johnston[7] for this reaction to become important in the stratosphere ($k^{II} \geq 6 \times 10^2$ M^{-1} s^{-1}). From our estimated processing rates however, this reaction is not significant even though k^{II} ~5×10^4 M^{-1} s^{-1} in 60 wt % acid at 219 K. The high solubility of HONO assumed by Burley and Johnston is the main reason for their calculated processing rates for HCl being high. The opposing variations in HONO and HCl solubility with wt % sulfuric acid, which was not anticipated by Burley and Johnston, is the main reason this reaction is not important in the stratosphere.

Our measured rate coefficients in the 60 wt % solutions are much higher than those in 50 wt %. Although it is not possible to substantiate mechanisms using kinetic measurements, this is consistent with the solubility measurements that suggest there is a change in the N(III) species from 50 to 60 wt %. Apparently the reaction of H_2ONO^+ with HCl/Cl^- is faster than the reaction of HONO with Cl^-. k^{II} in 70 wt % H_2SO_4 is higher yet at 215 K possibly indicating the presence of a third species, perhaps $NO^+HSO_4^-$. Another factor is the possible increase of k^{II} with acidity, as found for the reaction of HOCl with HCl in 49 to 67 wt % H_2SO_4.[40] k^{II} for HOCl + HCl increased about a factor of 20 over this range; k^{II} for HONO + HCl reported here increases by about a factor of 100 from 50 wt % to 70 wt % H_2SO_4 at 210 ± 5 K. The presence of a strong acid greatly affects the solubility and reactivity of HONO in solution as demonstrated by the null reaction in NaCl solution. This differs from the suggestion of Fenter et al.[11] where they suggested that ClNO could be formed from reaction of HONO with solvated chloride ions.

Conclusions

The effectiveness of this reaction under stratospheric conditions is limited primarily by the fact that HONO and HCl are not mutually highly soluble in sulfuric acid. Over the range of sulfuric acid content investigated here, the solubility of HONO increases with increasing wt % H_2SO_4, whereas the HCl solubility decreases as the acidity increases. Likewise, while HCl becomes more soluble in dilute sulfuric acid, HONO becomes less soluble. In addition, the relatively low reaction rate coefficients (less than the diffusion-limited value of $\sim 10^9$ M^{-1} s^{-1})[39] obtained from the measurements here, lead to a very limited effect of this reaction, and it can probably be ignored in the unperturbed stratosphere. Under certain volcanic conditions, the processing rate of HCl by the heterogeneous reaction with HONO can be comparable to that of reaction with OH, but it will require a better estimate of stratospheric [HONO] and detailed modeling calculations to determine its possible impact.

In summary, the heterogeneous reaction of HONO with HCl is apparently enhanced at the surface (with respect to the bulk rate), and we observed this in both wetted wall flow tube measurements and measurements on particles. For the conditions of our experiments, it appears that the surface specific component is expressed most at temperatures of 250 K and above; the data at the lowest temperatures can be described using a very small or nonexistent surface component.

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$$\Delta S_{\mathrm{HONO}} = \frac{z}{v_{\mathrm{ave}}} k_{\mathrm{ClNO}} S_{\mathrm{ClNO}} 3.6 \exp^{-k_{\mathrm{HONO}} z}$$

where v_{ave} is the average carrier flow velocity, k_{ClNO} is the first-order loss rate for ClNO obtained from ClNO uptake experiments, 3.6 is the sensitivity factor between the signals due to ClNO and HONO (S_{ClNO} and S_{HONO}, respectively), and k_{HONO} (cm^{-1}) is the first-order loss rate for HONO we are seeking. k_{HONO} was then obtained by an iterative procedure. In our analysis, z was measured from a reference point that was ~2 cm upstream of the end of the liquid. This equation is a crude way to take into account the reverse reaction. Note that the ΔS_{HONO} values calculated from this equation were comparable to those calculated from the equilibrium constant and the estimated asymptotic signal levels.

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