J. Phys. Chem. A **1997,** *101,* 4717−4725

Detailed Study of HOCl + HCl → Cl_2 + H_2O in Sulfuric Acid

D. J. Donaldson,*,[†] A. R. Ravishankara,[‡] and David R. Hanson*

Aeronomy Laboratory, National Oceanic and Atmospheric Administration, Boulder, Colorado, and Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, Colorado

Received: October 24, 1996; In Final Form: January 17, 1997[⊗]

Reactive uptake coefficients for HOCl as a function of [HCl] were measured in a rotating wetted-wall flow reactor for several sulfuric acid solutions containing between 49 and 67 wt % H_2SO_4 at 220 and 250 K. The solubility of HOCl in sulfuric acid solutions at 220 and 250 K was also measured. Using these measured solubilities, calculated HCl solubilities, and estimated diffusivities for HOCl, the second-order rate coefficients (k^{II}) in the liquid were extracted. At 250 K, k^{II} increases with increasing acid concentration, from 3×10^5 M^{-1} s^{-1} at 49 wt % acid to 5×10^6 M^{-1} s^{-1} at 67 wt %. It is suggested that the reaction may involve an initial protonation of HOCl, followed by reaction of H_2OCl^+ with Cl^-.

Introduction

The reactive uptake of HOCl onto ice and sulfuric acid solutions doped with HCl is thought to play a significant role in the activation of chlorine in the stratosphere.[1]

$$\mathrm{HOCl} + \mathrm{HCl} \rightarrow \mathrm{H_2O} + \mathrm{Cl_2} \tag{R1}$$

This reaction has been investigated in the laboratory by a number of groups.[2−5] Sources of HOCl in the stratosphere include heterogeneous hydrolysis of $ClONO_2$

$$\mathrm{ClONO_2} + \mathrm{H_2O} \rightarrow \mathrm{HNO_3} + \mathrm{HOCl} \tag{R2}$$

and the gas phase process,

$$\mathrm{ClO} + \mathrm{HO_2} \rightarrow \mathrm{HOCl} + \mathrm{O_2} \tag{R3}$$

Reactions such as R1 and R2 are important in the stratosphere because they transform reservoirs for active chlorine into more photochemically labile chlorine.

Accurate parameterization of the rates of these reactions is needed in atmospheric models to calculate the reaction probability, γ. Ideally, such models use a framework based on a mechanistic understanding of the reactions to predict the reaction probability as a function of temperature, water partial pressure, trace gas concentrations, and aerosol size. We have recently outlined a framework for such models[6a] which is briefly described here.

The uptake of a gas phase species into solution is governed by its physical solubility and by reaction (reversible or irreversible) in solution. The competition between diffusion of the species and its consumption *via* reaction will determine its distribution in the liquid phase. Analytical solutions of the continuity equation, including diffusion and reaction, have been worked out for many systems of interest.[6b,c] In the general case of a spherical droplet of radius a, γ for species X is given by[6a]

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{\omega}{4RTH_X\sqrt{kD_1}\,f(a/l)} \tag{1}$$

where α is the mass accommodation coefficient for species X, ω is the mean molecular speed, D_l is the liquid phase diffusion coefficient, k is the first-order loss rate coefficient, and H_X is the (effective) Henry's law constant for molecule X. The function $f(a/l) = \coth(a/l) - l/a$ depends upon the ratio of the radius a of the liquid particle to the "reactodiffusive length" $l = (D_l/k)^{1/2}$ of X;[6] in the bulk experiments described here, $f(a/l) = 1$.

The reaction of HOCl with HCl in 60 wt % sulfuric acid has been studied previously[3,4] using the same methods as those employed here. The rate coefficient for R1 in ~60 wt % sulfuric acid was determined at two temperatures, 200−205 K ($k^{II} = 1.6 \times 10^5$ M^{-1} s^{-1}) and 251 K ($k^{II} = 1.4 \times 10^6$ M^{-1} s^{-1}). These results suggest an activation energy of ~5 kcal mol^{-1} for the reaction at this acid concentration. Earlier studies of Cl_2 hydrolysis in solutions, with $[H^+] < 0.1$ M, derived a value for the third-order rate coefficient of 1.8×10^4 M^{-2} s^{-1} for the process

$$\mathrm{H^+} + \mathrm{Cl^-} + \mathrm{HOCl} \rightarrow \mathrm{H_2O} + \mathrm{Cl_2} \tag{R1$'$}$$

at 293 K.[5a,b] HCl is thought to be present primarily as Cl^- in the 49−67 wt % solutions,[14] and the concentration of Cl(−I) in solution is equal to $[Cl^-] + [HCl]$. To simplify the discussion, we use [HCl] to denote [Cl(−I)].

There is a lack of measurements of R1 in strong sulfuric acid solutions and the second-order liquid phase rate coefficient for R1 (k^{II}) is currently assumed to be independent of the acid content of the liquid.[7] The results presented below show that this assumption is not valid.

Here, we examine the reaction of HOCl with HCl (R1) in detail. Measurements of HOCl solubilities and reaction probabilities for R1 over a wide range of sulfuric acid concentrations (50−75 wt %) at 250 and 220 K are presented. A possible reaction mechanism is suggested, and a formulation of k^{II} as a function of acid content is presented. An improved methodology for calculating γ for reaction 1 is also presented.

Experimental Section

(a) Procedure. The bulk uptake measurements were performed using the rotating wetted-wall (RWW) flow reactor (inner diameter of 1.84 cm), described in detail previously.[8] Approximately 1 mL of sulfuric acid solution was placed inside the RWW. During an experiment, the acid concentration was kept constant by maintaining a partial pressure of water equal to the vapor pressure of water for that acid concentration.[9a,14]

[†] Permanent address: Department of Chemistry, University of Toronto, Toronto, Ontario Canada M5S 1A1.

[‡] Also at Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO.

[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1997.

S1089-5639(96)03315-4 CCC: $14.00

Following most experiments, a sample of the solutions was titrated with a standardized NaOH solution; the acid content was within 0.5 wt % of the concentration estimated from the water partial pressure and temperature. Some acid samples were used repeatedly: after a set of uptake measurements, the H_2O content of the liquid was varied (by setting a new partial pressure of H_2O and allowing sufficient time, ~30 min, for the "stirred" acid solution and the gas phase H_2O to equilibrate) and a new set of uptake measurements were performed. Several acid concentrations were used in this study: 49, 52, 54, 56.5, 58, 62.5, 65, 67, 70, and 75 wt % at 250 K and 58, 60, 63, 67, 70, and 75 wt % at 220 K (uncertainty of the H_2SO_4 content of the solutions is ±0.5 wt %.)

Gas phase first-order loss rate coefficients (k_g) for HOCl were measured in the wetted-wall flow reactor in an excess of HCl. HOCl, prepared by reaction of HF with $Ca(OCl)_2$ powder,[3,4] was entrained in a flow of He and introduced into the main He flow through a movable injector. By moving the injector, the exposure to the solution was varied, and k_g was obtained. HCl and H_2O were introduced into the main He flow upstream of the rotating wetted wall. Because HCl was added to the solutions from the gas phase, saturation of the solutions must be ensured. By comparing [HCl] exiting the RWW to [HCl] entering the RWW (monitored by diverting the HCl flow around the RWW), we could determine when the solutions were saturated. Note that excess gas phase HCl does not guarantee that the liquid phase loss for HOCl is pseudo first-order (discussed further below and in the Appendix.)

HOCl, HCl, and Cl_2 were monitored using a chemical ionization mass spectrometer (CIMS), as described previously.[3,4,10] SF_6^- was used as the ionic reagent in the CIMS flow tube for most of the kinetic runs. The signal at 143 amu, the SF_5O^- product ion formed in the $SF_6^- + HOCl$ reaction, was found to have a significant contribution from SF_4Cl^- when [HCl] was large (this appeared to be due to a reaction between SF_5^- and HCl; an ion−molecule reaction rate coefficient of 1.0×10^{-10} cm^3 s^{-1} would explain our observations.) Therefore, the $F^- + HOCl \rightarrow ClO^- + HF$ reaction was also used on occasion to monitor HOCl. The chemical ionization mass spectrometer was calibrated using known HCl concentrations, and the SF_5Cl^-/SF_6^- signal ratio was used to calculate the absolute HCl concentration.[3,4] The range of HCl partial pressures, p_{HCl}, was $\sim(3 \times 10^{-10})-(3 \times 10^{-7})$ atm. p_{HOCl} (typically 10^{-9} atm) was estimated by comparing the SF_5O^- signal to the calibrated signal for HCl at 162 amu (SF_5Cl^-) and applying the ~5 factor difference in sensitivity (*i.e.*, the ratio of the reaction rate coefficients.[10])

The total pressure was typically 1 Torr, though measurements at both larger (up to 3 Torr) and smaller (down to 0.5 Torr) pressures were performed. The majority of the gas was He while water partial pressure was a maximum of 0.2 Torr for 49 wt % acid at 250 K. The average flow velocity was typically ~1000 cm s^{-1}, and the total mass flow rate was in the range 3−4 std cm^3 s^{-1}. The RWW was rotated between 0 and ~3 rpm for the reactive uptake measurements. No dependence on rotation rate was observed for the measured reaction probabilities except for low p_{HCl} results for 67 wt % acid: at 250 K and for $p_{HCl} = 3 \times 10^{-9}$ atm the reaction probability decreased by about a factor of 2 when the RWW was stopped. A much smaller decrease (~15%) was observed at 250 K for $p_{HCl} = 2 \times 10^{-8}$ atm, and at higher p_{HCl} γ did not depend on rotation rate. The dependence on rotation rate is most likely due to the stirring of the solution. In these cases, it was discovered that the solution [HOCl] was larger than [HCl] and consequently pseudo-first-order loss rate conditions for HOCl were not achieved and physical agitation of the solutions would be expected to influence γ. Measurements when solution [HOCl] was greater than 0.5 × [HCl] were not included in the analysis. From simple modeling calculations (see Appendix) we predict less than a 10% effect on the measured γ when [HOCl] is less than 0.5 × [HCl] (compared to the case when [HOCl] ≪ [HCl].)

Nonreactive uptake (without HCl present) of HOCl in H_2SO_4 solutions was also studied and HOCl solubility was determined.[3,4] The Henry's law coefficient H_{HOCl} was determined at 250 K for several acid concentrations by measuring the total uptake of HOCl into a continuously stirred acid solution.[4] The parameter $H_{HOCl}(D_l)^{1/2}$ was determined at 220 K for three H_2SO_4 solutions by measuring the time-dependent HOCl uptake onto quiescent liquids.[3]

Measurements of the reaction probability of HOCl on sulfuric acid aerosol particles doped with HCl were performed at 250 K. The experimental procedure is identical to that described by Hanson and Lovejoy[4] except the aerosol particles were composed of 67 wt % H_2SO_4 and $\sim 6 \times 10^{-5}$ M HCl (*i.e.*, the aerosol particles were exposed to an HCl partial pressure of $\sim 1 \times 10^{-6}$ atm) and γ for HOCl was measured as a function of particle radius.

(b) Data Analysis. The measured decrease in [HOCl] as a function of injector position was fitted to a first-order decay, and then transformed into a loss rate coefficient (k_g) using the calculated average flow velocity in the flow reactor. This loss rate was "corrected" for gas phase diffusional loss[11a] (typically <20%, however, for bulk experiments with large uptakes, $\gamma \sim 0.1$, up to ~150%). For bulk measurements γ was calculated[11b] by dividing k_g by ω/d where ω is the mean molecular speed and d is the inner diameter of the flow reactor.[12] For the aerosol experiments γ was obtained by dividing k_g by the first-order collision rate with the aerosol particles.[4] Gas phase diffusion coefficients for HOCl-in-He and H_2O (p(Torr) × D_g = 339 and 81 Torr cm^2 s^{-1}, respectively, at 250 K) were estimated[13] using the Lennard-Jones parameters of ClO for HOCl.

The liquid phase first-order rate coefficient k is given by k^{II}[HCl] and [HCl] = $H^*_{HCl}p_{HCl}$, where H^*_{HCl} is the effective Henry's law constant for HCl (see note 14 in ref 4 for an explanation of effective Henry's law constants.) Thus, from eq 1 and for $\gamma \ll \alpha$, γ for HOCl is proportional to $(p_{HCl})^{1/2}$ if the reaction takes place in the bulk solution. Thus, plots of log γ *vs* log p_{HCl} should yield slopes of 0.5. Alternatively, plots of $1/\gamma$ *vs* $1/(p_{HCl})^{1/2}$ should be linear with intercepts equal to $1/\alpha$ (eq 1).

The inverse of the reaction probability $1/\gamma$ was found to be linearly proportional to $1/(p_{HCl})^{1/2}$. The slopes of these plots were used to extract k^{II}. Inserting $k = k^{II}H^*_{HCl}p_{HCl}$ and $f(a/l)$ = 1 into eq (1), the slopes of linear regressions to $1/\gamma$ *vs* $1/(p_{HCl})^{1/2}$ are related to solubilities, D_l, and k^{II} *via*

$$\text{slope} = \frac{\omega}{4RTH_{HOCl}\sqrt{k^{II}H^*_{HCl}\,D_l}} \qquad (2)$$

The values of H^*_{HCl} were taken from the calculations of Carslaw *et al.*[14] Values of H_{HOCl} were taken from the calculations of Huthwelker *et al.*[15] for acid concentrations less than 60 wt %, and interpolated from the measured solubility data presented here in the range 60−75 wt % (see below.) Values of D_l for HOCl were taken to be 1.1 times that of Huthwelker *et al.*[15] (this calculation for D_l was about 10% less than the measured value for 60 wt % acid[4]). The values of all parameters used in the analysis are listed in Table 1.

TABLE 1: Henry's Law Solubilities and Parameters Used To Determine k^{II}

	250 K				220 K		
H_2SO_4 wt %	measured H_{HOCl} M atm^{-1} [a]	H_{HOCl} enhanced (Table 5)	D_l (ref 15) 10^{-7} cm^2 s^{-1}	H^*_{HCl} (ref 14), M atm^{-1}	measured[b] $H_{HOCl}\sqrt{D_l}$	calculated,[b,c] $H_{HOCl}\sqrt{D_l}$	H^*_{HCl}
49		3770	8.7	33800			
52	2500	2900	7.9	13100			
54		2500	7.3	6800			
56.5		1980	6.6	2900			
58		1700	6.2	1740	(9)[e]	8.4	2.8×10^4
60	1400[d]	1500		1000	7.1	6.4	1.2×10^4
62.5	1100	1210	4.9	340			
63					(4.6)[e]	4.2	3500
65	1100	1060	4.2	130			
67	900	1000	3.6	60	2.7	2.6	
70	1000	940					
75					0.9	0.73	

[a] Estimated uncertainty is ±25%. [b] In units of M atm^{-1} cm $s^{-1/2}$. Estimated uncertainty in the measured values is ±30%. [c] Calculated using the enhanced H_{HOCl} from Table 5 and D_l from Huthwelker.[15] These values are 15−20% lower than the measured values. The measured values were used in the calculation of k^{II} in Table 2. [d] From ref 4. Actual conditions: 59.5 wt % and 251 K. [e] Extra- and interpolated from the measured values.

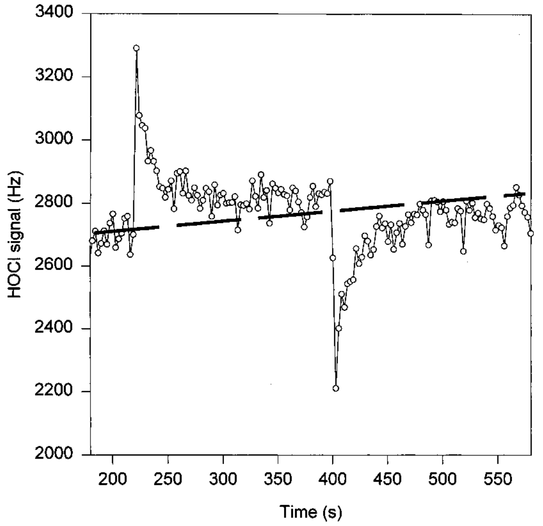

Figure 1. Results of nonreactive uptake experiment at 250 K, in 62.5 wt % sulfuric acid. Both an uptake (negative-going signal) and a desorption (positive-going signal) measurement are shown. The integrated area between the curves and the interpolated unperturbed signal (dashed line) is proportional to the Henry's law coefficient of HOCl. A slow increase with time in [HOCl] from the source is evident.

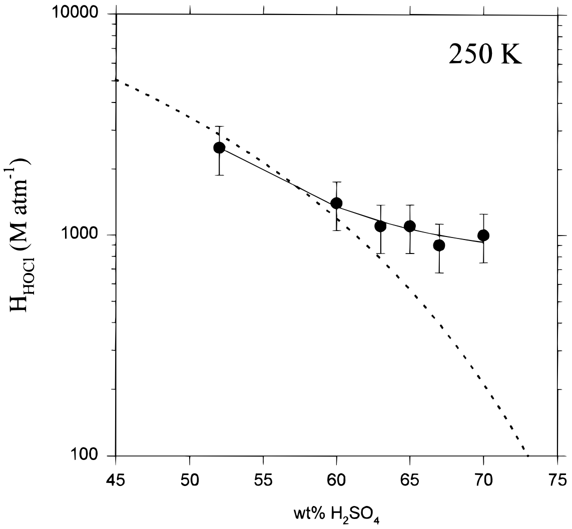

Figure 2. Measured Henry's law constants for HOCl in sulfuric acid, as a function of acid concentration. The dashed line is from the model of Huthwelker *et al.*[15] and the solid line is a fit to the data—see text for details.

Results

(a) Solubility of HOCl in H_2SO_4. Figure 1 displays a representative nonreactive HOCl uptake experiment for 62.5 wt % acid at 250 K. Several uptake and evaporation cycles for HOCl were performed for a number of acid concentrations. In all cases, H_{HOCl} derived from uptake measurements was the same as that derived from evaporation measurements. (Note that, in some runs, the very first exposure of HOCl to the liquid resulted in a large and irreversible uptake of HOCl, indicating the presence of a small amount of a dissolved impurity in some of the solutions.) The measured results are presented in Table 1 where the ±25% uncertainty[4] reflects the combined precision and estimated systematic error. Shown in Figure 2 are the measured values plotted *vs* wt % at 250 K; the dashed line shows the calculated values of Huthwelker *et al.*[15] The measured H_{HOCl} in 62.5−70 wt % acid are higher than those calculated using the model of Huthwelker *et al.*[15] The measured values of $H_{HOCl}\sqrt{D_l}$ at 220 K are also larger than the model prediction.

The measured values divided by the calculated values defines an enhancement factor and a fit of this *vs* H_2SO_4 content resulted in the equation

$$\text{enhancement factor} = 1 + 1.052 \times \exp(0.273 \times (\text{wp} - 65.66)) \quad (3)$$

where wp is wt % H_2SO_4. Thus H_{HOCl} (solid line in the figure) is obtained by multiplying the calculated values[15] by eq 3. This is a strictly empirical approach; our object is to obtain H_{HOCl} for a given H_2SO_4 content. The measured $H_{HOCl}\sqrt{D_l}$ at 220 K and $H_{HOCl}\sqrt{D_l}$ calculated according to this procedure and D_l taken from Huthwelker *et al.*[15] are also listed in Table 1. The enhancement factor is taken to be independent of temperature. The calculated values (eq 3) lie within 15% of the measured values at 220 K.

(b) Reactive Uptake and Kinetics of HOCl + HCl. The measured first-order loss rates for HOCl were used to calculate γ, as outlined above. The growth of Cl_2 was consistent with the observed loss of HOCl. A relatively large Cl_2 background arising from the HOCl source precluded extracting good kinetic data from the Cl_2 growth curves.

Figures 3 and 4 display representative plots of log γ *vs* log p_{HCl} for 250 and 220 K, respectively. For the most part, γ varies as $p_{HCl}^{1/2}$ as expected, with slopes of linear regressions to the data in the log−log plots ranging from 0.4−0.55. γ depends on the sulfuric acid content, in general decreasing with increasing H_2SO_4 concentration. Also, for a given p_{HCl} and acid

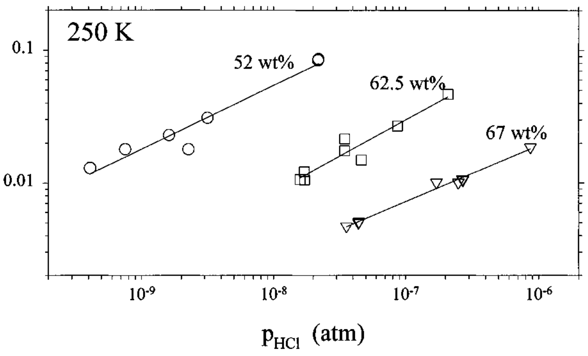

Figure 3. Representative results showing the reactive uptake of HOCl as a function of HCl pressure, at 250 K. The slopes of the 52, 62.5, and 67 wt % data are 0.48, 0.55, and 0.43, respectively.

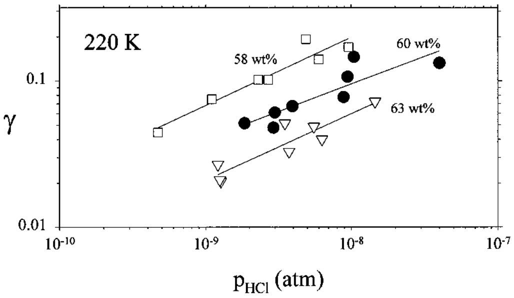

Figure 4. Results of reactive uptake experiments at 220 K. The slopes of the 58, 60, and 63 wt % data are 0.46, 0.38, and 0.45, respectively.

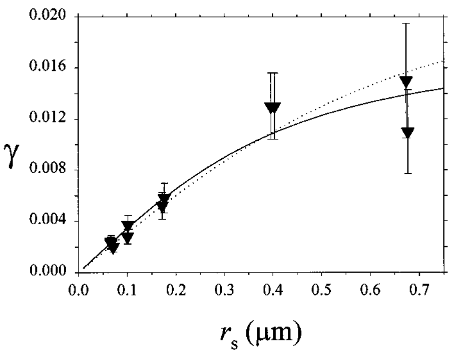

Figure 5. Measured reaction probability on 67 wt % H_2SO_4 particles at 250 K plotted against particle radius. The dashed and dotted curves are fits of the data to eq 4.

concentration, γ is larger by almost an order of magnitude at 220 K than it is at 250 K. Uptake experiments performed with 70 and 75 wt % acid showed small losses for HOCl, and pseudo-first-order loss rate conditions for HOCl in solution could not be ensured (note that the solubility of HOCl is much greater than the solubility of HCl in these solutions.) A portion of the low p_{HCl} data for the 62.5, 63, 65, and 67 wt % solutions was also not included in the analysis (at 220 K, none of the 65 and 67 wt % data was acceptable).

The measured γ on 67 wt % sulfuric acid aerosol is plotted as a function of particle size (surface-area-weighted mean radius,[8] r_s) in Figure 5. γ increases nearly linearly with r_s for small particles and approaches a limiting value for large r_s. This is expected according to eq 1 which reduces to

$$\gamma \approx \Gamma_b f(r_s/l) \tag{4a}$$

$$\Gamma_b = (4RT/\omega)H_{HOCl}(D_l k)^{1/2} \tag{4b}$$

when $\Gamma_b f(r_s/l) \ll \alpha \sim 1$ (and $a = r_s$). The solid curve is a fit to the data according to eq 4 resulting in values of $\Gamma_b = 0.019$ and $l = 0.18$ μm. The dashed curve is a fit with Γ_b fixed at 0.026, the value predicted from the 67 wt % bulk data at 250 K; this results in a value for l of 0.28 μm. Using this latter value and the definition of $l = (D_l/k)^{1/2}$, the first-order loss rate coefficient for HOCl is $k = D_l/l^2 = 460$ s^{-1}; dividing by the estimated [HCl] (6×10^{-5} M) results in a second-order rate coefficient in 67 wt % acid at 250 K of $\sim 8 \times 10^6$ M^{-1} s^{-1}. This compares favorably (within a factor of 2) with the result derived from the bulk measurements. A more accurate comparison between the bulk and aerosol measurements is not warranted (as was done in ref 4.) Accurately measuring $l \geq \sim 0.3$ μm is difficult because our present technique for sizing of the particle samples (UV light extinction measurements between 0.2 and 0.4 μm) becomes uncertain above $r_s = 0.6$ μm.

TABLE 2: Liquid Phase Second-Order Rate coefficients

wt % acid	slope^a (250 K), eq 2	k^{II} (250 K),^{b} M^{-1} s^{-1}	slope^a (220 K), eq 2	k^{II} (220 K),^{b} M^{-1} s^{-1}
49	0.0011	2.8×10^5		
52	0.0018	5.3×10^5		
54	0.0020	1.2×10^6		
56.5	0.0041	1.2×10^6		
58	0.0044	2.4×10^6	4.2×10^{-4}	4.3×10^5
60		$1.4 \times 10^{6\,c}$	8.0×10^{-4}	4.4×10^5
62.5	0.011	4.7×10^6		
63			0.0016	9.1×10^5
65	0.018	7.5×10^6		
67	0.04	4.9×10^6		

[a] In units of atm$^{-1/2}$. [b] Uncertainties are +100, −50%. [c] Fom ref 4.

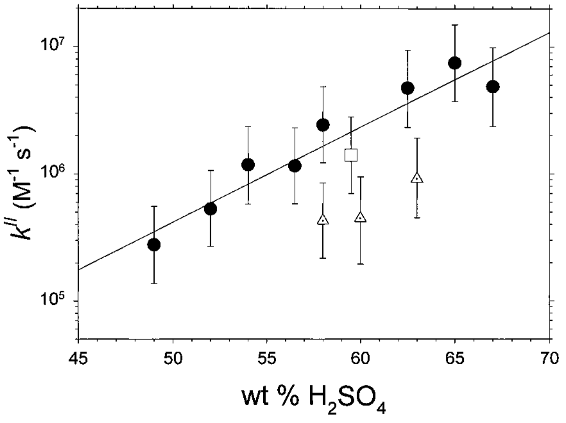

Figure 6. The measured second-order rate coefficients for the HOCl + HCl reaction, plotted as a function of wt % H_2SO_4: 250 K, filled circles; 220 K, dotted triangles. The open square is the measurement at 251 K from ref 4. A linear regression to the data at 250 K is shown: $\log_{10} k^{II} = 1.884 + 0.0747wp$ with wp in wt %.

Shown in Table 2 and Figure 6 is k^{II} calculated as described above using the parameters listed in Table 1. The values of the slopes (eq 2) are also listed in Table 2. Note the strong dependence of k^{II} on [H_2SO_4] at 250 K in the 49−67 wt % range. The measured rate coefficients at 220 K are also consistent with this trend.

The uncertainties in k^{II} are (+100, −50%) and were estimated by summing (in quadrature) the estimated errors in the values of $(H_{HOCl})^2$ (+56, −36%), H^*_{HCl} (+30, −23%), D_l (+33, −25%), and p_{HCl} (+25, −20%). Twice the precision in measuring γ a number of times n (*i.e.*, $\sim 2 \times (15\%/n^{1/2}) = 9\%$ for $n \sim 10$) is small compared to this estimated uncertainty. The uncertainties in the calculated H^*_{HCl} and D_l for HOCl were estimated by comparing to measured values (HCl solubilities from 45−60 wt % of refs 3 and 4 and HOCl diffusivity of ref 4 at 60 wt %.) Note that the uncertainties in the calculated H^*_{HCl} and D_l are not known outside of these ranges. We cannot assess the possible additional uncertainty in these quantities until a comparison to measurements over a wide range of conditions is made.

Discussion

(a) HOCl Solubility. Our measured solubilities for HOCl are greater than those predicted by the model of Huthwelker *et al.*[15] for acid content >60 wt %. The model is a fit to measurements at acid concentrations less than 60 wt % and predicts a steady decrease in H_{HOCl} with increasing acid concentration. The model considers only the *physical* solubility of HOCl; protonation is not included. The higher measured values could be partly due to protonation of HOCl at high acid concentrations. We define a thermodynamic protonation equilibrium constant K_{eq} to be the inverse of the H_2OCl^+ acid constant:

$$K_{eq} = \frac{a_{H_2OCl^+}}{a_{HOCl}a_{H^+}} = \frac{[H_2OCl^+]}{[HOCl][H^+]}\frac{f_{H_2OCl^+}}{f_{HOCl}f_{H^+}} \qquad (5)$$

where a_i and f_i represent the activity and molar activity coefficient, respectively, of component i. An effective Henry's law constant H^*_{HOCl} can be defined which is a function of acid strength

$$H^*_{HOCl} = ([HOCl] + [H_2OCl^+])/p_{HOCl} = H_{HOCl}\,(1 + [H^+]K_{eq}f_{H^+}f_{HOCl}/f_{H_2OCl^+}) \qquad (6)$$

If K_{eq} is sufficiently small, protonation is not important until high acid concentrations; this is apparently the case for HOCl in concentrated H_2SO_4.

Although protonated HOCl has not been detected in solution, it has been reported in the gas phase *via* mass spectrometry,[17] and its existence in/on amorphous solids has been inferred from infrared spectra of matrix-isolated $ClONO_2/H_2O$ mixtures.[18] On the basis of these spectra, Sodeau *et al.*[18] proposed H_2OCl^+ as an intermediate in chlorine nitrate hydrolysis. An alternative interpretation, consistent with the present work, is that some of the HOCl formed in the hydrolysis is protonated by H^+ from dissociated HNO_3 product. Protonated HONO has also been reported in sulfuric acid solutions of 70−90 wt % acid.[19] It is likely that HOCl becomes protonated to some extent in strong acid solutions.

Note that the enhancement in the solubility over that calculated using a simple Setchenow dependence[15] is not likely to be due only to protonation (*i.e.*, the last term in parentheses in eq 6 is likely to be small compared to one.) If the enhancement in the HOCl solubility were entirely due to protonation, then the concentrations of $[H_2OCl^+]$ and [HOCl] would be approximately equal in 65 wt % acid (where from Figure 2 the enhancement factor is ∼2.) The overall rate coefficient k^{II} would then be expected to be about one-half of the diffusion-limited value of 3×10^8 M^{-1} s^{-1} (assuming the rate coefficient for $H_2OCl^+ + Cl^-$ is diffusion limited, see R4 and R5 below.) Because the measured k^{II} in 65 wt % acid is much lower than the diffusion limited value, HOCl is not likely to be primarily in protonated form in these solutions. The reason the measured H_{HOCl} is greater than the predicted values[15] may be due to a rejection of higher order terms in the model.[15]

(b) Kinetic Analysis and Mechanistic Implications. The results shown in Figure 6 indicate a strong dependence of the reaction rate coefficient on acid concentration at 250 K. At this temperature, there is a 20-fold increase in k^{II} as the acid concentration increases from 49 to 65 wt %. The increase in k^{II} with acid content suggests that the reaction may involve a protonation step followed by reaction with Cl^- (we now explicitly denote the dissolved HCl as Cl^-.) This is the pathway

$$HOCl + H^+ \xleftrightarrow{k_4,\, k_{-4}} H_2OCl^+ \qquad (R4)$$

$$H_2OCl^+ + Cl^- \xrightarrow{k_5} Cl_2 + H_2O \qquad (R5)$$

denoted (4) → (2) → (1) by Eigen and Kustin.[5a] Note that the hydrolysis of Cl_2 (reverse of R5) can be neglected for the conditions of our experiment. According to this mechanism, the HOCl loss rate in the liquid is

$$\frac{d}{dt}[HOCl] = -k_4[HOCl][H^+] + k_{-4}[H_2OCl^+] \qquad (7)$$

Assuming a steady state for $[H_2OCl^+]$,

$$[H_2OCl^+]_{ss} = \frac{k_4[HOCl][H^+]}{k_{-4} + k_5[Cl^-]} \qquad (8)$$

and solving for the pseudo-first-order loss rate coefficient for HOCl, we obtain

$$k = \frac{k_4[H^+]}{k_{-4} + k_5[Cl^-]}k_5[Cl^-] \qquad (9)$$

Under the conditions of the present experiments, it is likely that $k_{-4} \gg k_5[Cl^-]$. The maximum Cl^- concentration in our experiments can be estimated from the maximum possible value of $H^*_{HCl}p_{HCl} = (10^4)(10^{-8}) = 10^{-4}$ M. Taking a diffusion-limited value for k_5 (∼3×10^8 M^{-1} s^{-1} at 250 K in 50−70 wt % H_2SO_4), we obtain a maximum value for $k_5[Cl^-]$ of ∼3×10^4 s^{-1}. Since we expect $k_4/k_{-4} = K_{eq}\, f_{H^+}f_{HOCl}/f_{H_2OCl^+} \ll 1$ (see below) and k_4 to be large, k_{-4} is almost certainly $\gg 3 \times 10^4$ s^{-1}. Thus we can simplify the expression above to

$$k \approx \frac{k_4[H^+]}{k_{-4}}k_5[Cl^-] \qquad (10)$$

This equation yields a straightforward dependence for k and γ on $[Cl^-]$ and on $[H^+]$, as is observed for 49−67 wt % solutions. Note that if k_{-4} were not $\gg k_5[Cl^-]$, this straightforward dependence would not have been observed. From this expression, the values of $k^{II} = k/[Cl^-]$ in Figure 6 and Table 2 are given by

$$k^{II} \approx \frac{k_4[H^+]}{k_{-4}}k_5 \qquad (11)$$

A similar expression can be derived assuming an initial attack by Cl^- on HOCl, as proposed by Eigen and Kustin[5a] and for much lower acid concentrations (the pathway they denote as (4) → (3) → (1)):

$$HOCl + Cl^- \xleftrightarrow{k_6,\, k_{-6}} HOCl_2^- \qquad (R6)$$

$$HOCl_2^- + H^+ \xrightarrow{k_7} Cl_2 + H_2O \qquad (R7)$$

The first-order rate coefficient for HOCl loss is

$$k = \frac{k_6[Cl^-]}{k_{-6} + k_7[H^+]}k_7[H^+] \qquad (12)$$

For $k^{\mathrm{II}} = k/[\mathrm{Cl}^-]$ and $k_{-6} \gg k_7[\mathrm{H}^+]$, this reduces to

$$k^{\mathrm{II}} \approx \frac{k_6}{k_{-6}} k_7[\mathrm{H}^+] \qquad (13)$$

This is the same form as k^{II} (eq 11) derived for the protonation mechanism (R4−R5). Note that Eigen and Kustin[5a] considered the protonation mechanism to be too slow to contribute to their measurements on the basis of thermodynamic calculations[20] that suggested the "extreme unlikelihood" of finding H_2OCl^+ in solution. That argument might not be valid in the strong acid solutions studied here. Note that our kinetic results do not help us choose between these two mechanisms. It is reasonable, however, to suggest that R4−R5 is a likely pathway in strong acids.

The dependence of k^{II} on acid content can be understood by using the concept of the effective acidity in strong acid solutions, first proposed by Hammett.[21] Much work has been carried out on the reactions of organic weak bases in strong acids (such as sulfuric acid),[22,23] and these reactions typically follow a mechanism similar to that given by R4−R5. Our analysis of the variation of k^{II} with acidity is based on this body of work.

First, we introduce the ratio $k_4/k_{-4} = [\mathrm{H_2OCl^+}]/[\mathrm{H^+}][\mathrm{HOCl}] = K_c$ (the concentration equilibrium constant[37]) into the expression for the thermodynamic protonation constant of HOCl (eq 5):

$$K_{\mathrm{eq}} = \frac{[\mathrm{H_2OCl^+}]}{[\mathrm{HOCl}][\mathrm{H^+}]} \frac{f_{\mathrm{H_2OCl^+}}}{f_{\mathrm{H^+}} f_{\mathrm{HOCl}}} = \frac{k_4}{k_{-4}} \frac{f_{\mathrm{H_2OCl^+}}}{f_{\mathrm{H^+}} f_{\mathrm{HOCl}}} \qquad (14)$$

Replacing eq (14) in eq (11) and taking logarithms,

$$k^{\mathrm{II}} = K_{\mathrm{eq}} \frac{f_{\mathrm{H^+}} f_{\mathrm{HOCl}}}{f_{\mathrm{H_2OCl^+}}} [\mathrm{H^+}] k_5 \qquad (15)$$

$$\log k^{\mathrm{II}} = \log K_{\mathrm{eq}} + \log \frac{f_{\mathrm{H^+}} f_{\mathrm{HOCl}}}{f_{\mathrm{H_2OCl^+}}} + \log\, [\mathrm{H^+}] + \log k_5 \qquad (16)$$

Following the "excess acidity" analysis of Cox and Yates,[24−26]

$$\log \frac{f_{\mathrm{H^+}} f_{\mathrm{HOCl}}}{f_{\mathrm{H_2OCl^+}}} = m^* \log \frac{f_{\mathrm{H^+}} f_{\mathrm{B^*}}}{f_{\mathrm{B^*H^+}}} = m^* X \qquad (17)$$

where B^* represents a hypothetical standard reference base. This states that the ratios of activity coefficients for protonation reactions in strongly acidic media are simply related to one another, *via* the parameter m^*. Note that m^* as used here is slightly different from that defined by Cox and Yates.[24,25] Using this definition of X and rearranging,

$$\log k^{\mathrm{II}} = \log K_{\mathrm{eq}} + m^* X + \log[\mathrm{H^+}] + \log k_5 \qquad (18)$$

$$(\log k^{\mathrm{II}} - \log[\mathrm{H+}]) = (\log K_{\mathrm{eq}} + \log k_5) + m^* X$$

$$\log(k^{\mathrm{II}}/[\mathrm{H^+}]) = \log(K_{\mathrm{eq}} k_5) + m^* X \qquad (19)$$

A semilog plot of $(k^{\mathrm{II}}/[\mathrm{H^+}])$ *vs* X should yield a straight line with $K_{\mathrm{eq}} k_5$ as intercept. Such a plot is shown for the 250 K data in Figure 7, with values of X and $[\mathrm{H^+}]$ taken from Cox and Yates.[24,25b] The fit to a straight line is good, albeit over a fairly small range of X, implying that the mechanistic assumptions behind the analysis are valid. The resulting slope $m^* = 0.5$ is in the range predicted for protonation on oxygen.[24,25a] The intercept from this plot yields a value of ∼1800 for $K_{\mathrm{eq}} k_5$. Note that the 95% confidence levels indicate an uncertainty in the intercept of a factor of 5 (+400, −80%).

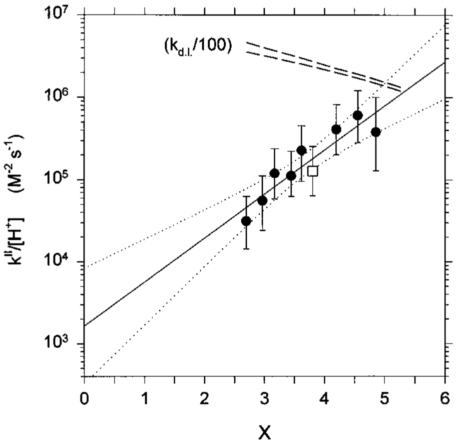

Figure 7. Logarithm of $k^{\mathrm{II}}/[\mathrm{H^+}]$ at 250 K plotted against the "X" parameter, a universal acidity function. A linear regression line and the 95% confidence limits are also shown (symbols as in Figure 6.) See text for details. Also shown (dashed lines) are the diffusion limited reaction rate coefficients $(k_{\mathrm{d.l.}})/100$, $k_{\mathrm{d.l.}} = 4\pi R^* D_l (6 \times 10^{20}\ \mathrm{M^{-1}\ s^{-1}})$, for $R^* = 6 \times 10^{-8}$ cm and D_l taken from Huthwelker *et al.*[15] (lower curve) and that from Williams and Long[16] (upper curve) normalized to $6 \times 10^{-7}\ \mathrm{cm^2\ s^{-1}}$ for 59.5 wt % acid at 250 K.[4]

Making the reasonable assumption that R5 is diffusion-limited ($k_5 = 3 \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$), the value of K_{eq} at 250 K is $\sim 10^{-5}\ \mathrm{M^{-1}}$. Alternatively, because k_5 is less than or equal to $3 \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$, our error limits imply a lower limit to K_{eq} of $(1/5)1800/3 \times 10^8 = 10^{-6}\ \mathrm{M^{-1}}$. This corresponds to an ideal solution, $[\mathrm{H^+}] = 0$, upper limit to ΔG^0 of $+7$ kcal mol^{-1} for the protonation reaction R4 at 250 K. This value is higher than that for methanol protonation (the ΔG^0 for the protonation of aqueous CH_3OH calculated from data in ref 27 is +1.2 kcal mol^{-1}) consistent with a smaller proton affinity for HOCl (an *ab-initio* determination of the gas phase proton affinity of HOCl[28] is 153 kcal mol^{-1}; ∼20 kcal mol^{-1} smaller than that for methanol.[29])

These arguments are consistent with the reaction mechanism involving an initial protonation followed by reaction of H_2OCl^+ with Cl^-. Reaction of H_2OCl^+ with molecular HCl, expected to be present in the most acidic solutions, could also occur.

(c) Temperature Dependence and Comparison to Previous Measurements. For the 58, 60, and 63 wt % results, there is about a factor of 4 difference between the k^{II} values at 250 and 220 K resulting in an estimate for the effective activation energy of 5 kcal mol^{-1} for the overall reaction, essentially the same as that estimated for 60 wt % between 202 and 250 K(∼5 kcal mol^{-1}.)[3,4]

Using an effective activation energy of 5 kcal mol^{-1}, we estimate the 293 K, $[\mathrm{H^+}] \rightarrow 0$ empirical rate coefficient to be $K_{\mathrm{eq}} k_5 \sim 10^4\ \mathrm{M^{-2}\ s^{-1}}$ (using $K_{\mathrm{eq}} k_5 = 1800$ at 250 K). This is of the same magnitude as the 293 K third-order reaction rate constant given by Eigen and Kustin[5a] for low acid concentrations ($1.8 \times 10^4\ \mathrm{M^{-2}\ s^{-1}}$). However, given the large uncertainty in the intercept in Figure 7 and the large differences in reaction conditions between the present work and that of ref 5, this agreement may be fortuitous.

Wang and Margerum[5b] measured the temperature dependence of $K_{\mathrm{eq}} k_5$ (their k_{-1}) from 273 to 303 K and obtained 6.5 kcal mol^{-1} for an effective activation energy for $K_{\mathrm{eq}} k_5$. Using this activation energy, the extrapolation of their results to 250 K results in a value of 2400 $\mathrm{M^{-2}\ s^{-1}}$ for $K_{\mathrm{eq}} k_5$. This is in good agreement with our value extrapolated to $[\mathrm{H^+}] = 0$. Wang and

TABLE 3: Comparison with Previously Reported Rate Coefficients

wt % H_2SO_4	T, K	rate coefficient	extrapolated value[a]	lit. value	ref
0	293	$K_{eq}k_5$[b]	1.0×10^4 M^{-2} s^{-1}	1.8×10^4 M^{-2} s^{-1}	5a
0	250	$K_{eq}k_5$	1800 M^{-2} s^{-1}	2400 M^{-2} s^{-1} [c]	5b
34	274	k^{II}	6×10^4 M^{-1} s^{-1}	8×10^4 M^{-1} s^{-1}	4
59.5	251	k^{II}	2.1×10^6 M^{-1} s^{-1}	1.4×10^6 M^{-1} s^{-1}	4
60	202	k^{II}	2.2×10^5 M^{-1} s^{-1}	1.6×10^5 M^{-1} s^{-1}	3

[a] Obtained from the fit of $\log_{10} k^{II}$ *vs* wt % shown in Figure 6 along with a 5 kcal mol^{-1} effective activation energy (see Table 4). [b] For the reaction sequence R4−R5 with K_{eq} from eq 14. Also could be the analogous expression for the reaction sequence R6−R7. See text for details. [c] Extrapolated to 250 K.

Margerum also presented evidence for an acid-assisted mechanism

$$HA + HOCl + Cl^- \rightarrow A^-{\cdot}H_2OCl^+{\cdot}Cl^- \rightarrow A^- + H_2O + Cl_2 \quad (R8)$$

The HSO_4^- ion was identified as one of the acids HA. Note that the extrapolation to $[H^+] = 0$ in Figure 7 also involves extrapolation to $[HSO_4^-] = 0$. The transition state, $A^-{\cdot}H_2OCl^+{\cdot}Cl^-$, is described by Wang and Margerum as involving a proton transfer to HOCl as Cl^+ is transferred to Cl^-. They point out that a sequence similar to R6−R7 is a two-step analog to R8. The reverse of R8, the base-assisted hydrolysis of Cl_2, was originally proposed by Lifshitz and Perlmutter-Hayman[5c] as a two-step process similar to the reverse of R6−R7. An alternative is that a sequence similar to R4−R5 is also a two-step analog to R8. As Wang and Margerum stated, one cannot determine which mechanism is operating from kinetics alone. However, it appears that the protonation mechanism R4−R5 should not be rejected from consideration.

Shown in Table 3 are the comparisons discussed above for $[H^+] = 0$ and comparison of the previously reported values for k^{II} in strong sulfuric acid solutions with values obtained by extrapolating the present results to the same conditions. The values of the extrapolated k^{II} are −25, +50, and +35% different than the previously reported values. As all these measurements are accurate to approximately +100/−50%, these discrepancies are not consequential. Indeed, the agreement is remarkable considering the extent of extrapolation (∼15 wt % and ∼25 K).

(d) Atmospheric Implications. The parameters determined here allow a calculation of the reaction probability for HOCl onto stratospheric sulfuric acid aerosols. Recent measurements[4] of the reaction probability of HOCl on 34 wt % sulfuric acid suggest that the mass accommodation coefficient α is close to unity, and we take α = 1 independent of temperature and H_2SO_4 content. k^{II} was taken to be a function of wt % (as determined at 250 K; see Figure 6) and a 5 kcal/mole effective activation energy was employed (see Table 4.) The solubility of HOCl was taken to be that of Huthwelker *et al.*[15] with the additional enhancement at high acidities (eq 3). Figure 8 displays the values of γ calculated using the equations and parameters in Tables 4−6 for 0.2 μm radius particles over a range of stratospherically important temperatures, assuming $p_{H_2O} = 3 \times 10^{-4}$ mbar and $p_{HCl} = 10^{-10}$ atm. For these conditions, a line is plotted to show temperature *vs* wt % H_2SO_4. The expected reaction probabilities are different than those assuming k^{II} is independent of acid content (dash−dot curve in the figure). The overall conclusions regarding the relative importance of the HOCl + HCl reaction under stratospheric conditions are not altered (*i.e.*, it is significant only in solutions with acid content <∼60 wt %). Note that the reaction probability for cold polar lower stratospheric conditions is significantly less than the previous calculation, which was based on an invalid assumption (k^{II} independent of $[H_2SO_4]$). Note also that the HCl solubilities of Carslaw *et al.*[14] are higher than the HCl solubility given in Table 4 for cold conditions (H_2SO_4 content <50 wt %), and using them results in a higher calculated γ.

The initial protonation mechanism proposed here is not dependent on sulfuric acid being the proton donor. In principle, *any* strong acid could initiate a reaction, for example, aqueous HNO_3 Type I PSC particles would be expected to exhibit similar chemistry. Also, the reactive uptakes of HOBr and HONO *via* reactions such as HOBr + HCl and HONO + HCl may also proceed through such a mechanism. If $[HNO_3]$ is high, the reaction $H_2OCl^+ + NO_3^-/HNO_3 \rightarrow H_2O/H_3O^+ + ClONO_2$ might take place, regenerating chlorine nitrate from HOCl. This is analogous to the $BrONO_2 + H_2O \leftrightarrow HOBr + HNO_3$

TABLE 4: Parameters and Equations for Calculating Reaction Probability of HOCl onto Sulfuric Acid Particles

parameter	expression	ref
α	1.0	4
D_l	9×10^{-9} [b]	
a_{H2O}	$p_{H_2O}/10^{(9.217-2190/(T-12.7))}$	7, 38
H^*_{HCl}	$\exp(6250/T - 10.414) \times (a_{H_2O})^{3.49}$	7, 38
k^{II}	$\exp(2.303 \times (6.08 - 1050/T + 0.0747wp))$[c]	this work
k	$k^{II}H^*_{HCl}p_{HCl}$	s^{-1}
wp	see Table 5	wt % H_2SO_4
HrootD	$H_{HOCl}(D_1)^{1/2}$ [d]	Table 6
adivl	$r_p(k/D_1)^{1/2}$	this work
f	1/tanh(adivl) − 1/adivl	6a, 7
Γ_{calc}	$2.25 \times 10^{-5}(T52.5k)^{1/2} \times$ HrootD	this work
γ	$1/(\alpha^{-1} + (\Gamma_{calc}\, f)^{-1})$	6a, 7

[a] Input parameters are p_{HCl}, p_{H_2O}, r_p in atm, mbar, and cm, respectively. [b] D_l varies with T and acid content; however, for a given p_{H_2O}, these variations approximately cancel resulting in a constant D_l for wp as a function of T. $D_l = 9 \times 10^{-9}$ is predicted for stratospheric conditions from the relation D_l = const$T$/viscosity[15] with the constant determined for 59.5% acid at 251 K.[4] Note that the calculated γ is insensitive to the value of D_l for stratospheric conditions. [c] Note that this expression for k^{II} is not valid beyond 65 wt % acid. The calculated γ for atmospheric conditions using this expression (Figure 8), however, is $\leq 10^{-4}$ and is not significant for atmospheric conditions. [d] Formulation for H_{HOCl} from Huthwelker *et al.*[15] along with the enhancement at high acid content shown here are detailed in Table 6.

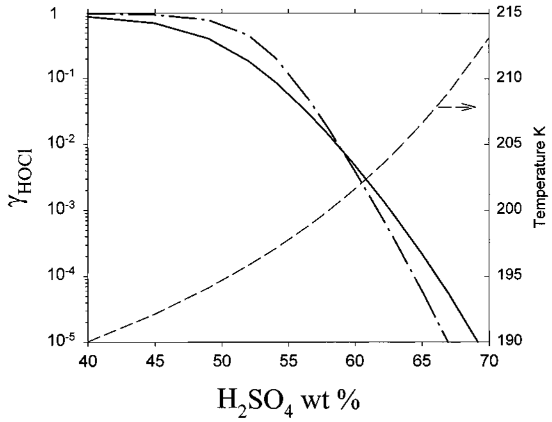

Figure 8. The predicted reactive uptake coefficient for HOCl + HCl on 0.2 μm aerosol particles, assuming $p_{H_2O} = 3.0 \times 10^{-4}$ mbar and $p_{HCl} = 10^{-10}$ atm. The short-dashed curve shows the variation of sulfuric acid aerosol composition with temperature (right axis) under these conditions (ref 9 and Table 4). The solid curve is the calculated reaction probability for HOCl + HCl using Tables 4, 5, and 6. The dash−dot curve is γ calculated as for the solid curve except assuming $k^{II} = 1.6 \times 10^5$ M^{-1} s^{-1} independent of acid content.

TABLE 5: Calculation of H_2SO_4 Content from T and p_{H_2O}. $Z = \ln(p_{H_2O}, \text{mbar})$

wt %	expression	ref
wp	$\frac{(-14.0508 + 0.708928 \times Z)T + 3578.6^{a}}{45.5374 + 1.55981 \times Z - 0.197298 \times T}$	33

[a] A fit using the p_{H_2O} *vs* wt % data of Giauque *et al.*[9] believed to be more accurate at low temperatures than the Gmitro and Vermeulen[30] data that Steele and Hamill[31] fitted to (see Massucci *et al.*[32]). Previous wp equation from ref 6a Table 3 results in a bias of 1−2 wt % with respect to the Giauque *et al.* data.[9] Extreme caution should be exercised in the use of this equation, *i.e.*, only for $10^{-4} < p_{H_2O} < 10^{-3}$ mbar, 40 < wp < 80, and 190 < T < 230 K. The maximum deviation of this equation from the Giauque *et al.* data[9] is 0.6 wt % with a root mean square deviation of 0.3 wt % for 195 < T < 230 K. At 190 K, the maximum deviation of this equation from the data[9] is 0.9 wt %.

TABLE 6: Solubility of HOCl. From Huthwelker *et al.*[15a]

parameter	expression	notes and refs
m	10.196wp/(100 − wp)	(wp to molal) only for pure sulfuric acid solutions
Hhuth	exp(6.4946 − m(−0.04107 + 54.56/T) −5862 × (1/298.15 − 1/T))	(molal atm^{-1})
rho	$1000 + C1m + C2m^{1.5} + C3m^2$	solution density (kg m^{-3})
$C1$	$123.64 - 5.6 \times 10^{-4}T^2$	
$C2$	$-29.54 + 1.814 \times 10^{-4}T^2$	
$C3$	$2.343 - 1.487 \times 10^{-3}T - 1.324 \times 10^{-5}T^2$	
conversion	(rho/1000)/(1+ m0.09808)	(molal to molar)
HM	(Hhuth) (conversion)	
H_{HOCl}	HM(1 + 1.052 exp(0.273 (wp − 65.66)))	enhancement factor at high acidities (this work)

reaction.[34] Note that the regeneration of $ClONO_2$ from HOCl and HNO_3 is not expected to be important in the atmosphere for the same reasons that regeneration of $BrONO_2$ could be ignored: the $[H_2O]/[HNO_3]$ ratio is so large that the equilibrium ratio $[XONO_2]/[HOX]$ is very small.

Acknowledgment. This work was funded in part by NOAA's Climate and Global Change Research program. We thank Professors A. J. Kresge and Robin A. Cox for helpful discussions about acidity functions, the reviewers for helpful comments, and I. K. Kim for taking the 220 K 58 wt % data. D.J.D. thanks NSERCC for a University Research Fellowship.

Appendix

A simple numerical procedure was used to solve simultaneously the equations

$$\frac{\partial C_1}{\partial t} = D_1 \frac{\partial^2 C_1}{\partial x^2} - k^{II} C_2 C_1$$
$$\frac{\partial C_2}{\partial t} = D_1 \frac{\partial^2 C_2}{\partial x^2} - k^{II} C_1 C_1 \qquad (20)$$

where C_1 and C_2 are the concentrations of components 1 and 2 in the liquid. After about 1 s of simulated time, steady state was achieved (with time step $dt = 10^{-6}$ s and $dx = 10^{-6}$ cm). A similar scheme was used in the appendices of refs 3 and 35. The finite-differencing scheme was forward time centered space, which is stable for parabolic equations such as eq 20 with $D_l dt/dx^2 < 0.5$.[36] The concentration at the surface was fixed for both C_1 and C_2, reflecting the fact that γ is much less than α (α ≈ 1) for our experimental conditions. D_l was chosen to be 4×10^{-7} cm^2 s^{-1} for both species, and k^{II} was chosen such that the quantity $k^{II}C_2(x = 0, t)$ was equal to 10 s^{-1}. In one run, $k^{II}C_2$ was held fixed at 10 s^{-1} for all x and t, and a reactodiffusive length of 2.00×10^{-4} cm was obtained for C_1, in excellent agreement with the theoretical value, $l = (4 \times 10^{-7}/10)^{1/2}$ cm, indicating the gradient at the surface is the expected value. In the next case, $C_2(x,t{=}0)$ was set equal to $2{\times}C_1(x,t{=}0)$ and both were allowed to change (decrease) with time. The gradient in C_1 was about 10% less than it would have been if C_2 was fixed at a constant value. (Note that, in the absence of surface reactions, γ is directly proportional to the gradient in the liquid at the surface.) Even for the case where $C_2(x,t{=}0)$ was equal to $C_1(x,t{=}0)$, the gradient in C_1 was only about 20% less than if C_2 were not allowed to vary. Therefore, we conclude that the measured reaction probability of component 1 is not affected by more than 10% if it is known that C_2 is at least 2 times C_1. Also note that the gas phase concentration of component 2 must be much greater than the gas phase concentration of component 1. Then the condition that $C_2(x{=}0,t)$ remains constant will be fulfilled.

References and Notes

(1) (a) Crutzen, P. J.; Muller, R.; Bruhl, Ch.; Peter, Th. *Geophys. Res. Lett.* **1992**, *19*, 1113. (b) Cox, R. A.; *et al. Geophys. Res. Lett.* **1994**, *21*, 1439.

(2) (a) Hanson, D. R.; Ravishankara, A. R. *J. Geophys. Res.* **1991** *96*, 17307. (b) Hanson, D. R.; Ravishankara, A. R. *J. Phys. Chem.* **1992**, *96*, 2682. (c) Abbatt, J. P. D.; Molina, M. J. *Geophys. Res. Lett.* **1992**, *96*, 7674. (d) Abbatt, J. P. D.; Molina, M. J. *J. Phys. Chem.* **1992**, *96*, 7674−7679. (e) Zhang, R.; Leu, M. T.; Keyser, L. *J. Phys. Chem.* **1994**, *98*, 13563.

(3) Hanson, D. R.; Ravishankara, A. R. *J. Phys. Chem.* **1993**, *97*, 12309.

(4) Hanson, D. R.; Lovejoy, E. R. *J. Phys. Chem.* **1996**, *100*, 6397.

(5) (a) Eigen, M.; Kustin, K. *J. Am. Chem. Soc.* **1962**, *84*, 1355. (b) Wang, T. X.; Margerum, D. W. *Inorg. Chem.* **1994**, *33*, 1050. (c) Lifschitz, A.; Perlmutter-Hayman, B. *J. Phys. Chem.* **1962**, *66*, 701.

(6) (a) Hanson, D. R.; Ravishankara, A. R.; Solomon, S. *J. Geophys. Res.* **1994**, *99*, 3615. (b) Danckwerts, P. V. *Trans. Faraday Soc.* **1951**, *47*, 1014. Danckwerts, P. V. *Gas-Liquid Reactions*; McGraw-Hill: New York, 1970. (c) Schwartz, S. E. in *Chemistry of Multiphase Atmospheric Systems*; Jaeschke, W., Ed.; Springer-Verlag: New York, 1986; 451.

(7) Ravishankara, A. R.; Hanson, D. R. *J. Geophys. Res.* **1996**, *101*, 3885.

(8) Lovejoy, E. R.; Huey, L. G.; Hanson, D. R. *J. Geophys. Res.* **1995**, *100*, 18775.

(9) (a) Giauque, W. F.; Hornung, E. W.; Kunzler, J. E.; Rubin, T. R. *J. Am. Chem. Soc.* **1960**, *82*, 62. (b) McDonald, J. E. *J. Geophys. Res.* **1965**, *70*, 1553. (c) Gable, C. M.; Betz, H. F.; Maron, S. H. *J. Am. Chem. Soc.* **1950**, *72*, 1445.

(10) Huey, L. G.; Hanson, D. R.; Howard, C. J. *J. Phys. Chem.* **1995**, *99*, 5001.

(11) (a) Brown, R. L. *J. Res. Natl. Bur. Stand. (U.S.)* **1978**, *83*, 1. (b) Howard, C. J. *J. Phys. Chem.* **1979**, *83*, 3.

(12) With liquid present, d is 0.88−0.90 cm and with the stirring rod present the effective inner diameter of the RWW flow reactor is $(0.89^2 - 0.25^2)^{1/2} = 0.85$ cm. Note that the presence of the ∼0.5 cm o.d. stirring rod may significantly compromise the cylindrical symmetry requirement of the diffusion correction procedure.[11a] This is expected to be important for large corrections. In these experiments, there are only a small number of measurements with corrections >20%. These have additional uncertainty included in the extracted reaction probabilities.

(13) (a) Mason, E. A.; Monchick, L. *J. Chem. Phys.* **1962**, *36*, 2746. (b) Monchick, L.; Mason, E. A. *J. Chem. Phys.* **1961**, *35*, 1676.

(14) Carslaw, K. S.; Clegg, S. L.; Brimblecombe, P. *J. Phys. Chem.* **1995**, *99*, 11557.

(15) Huthwelker, T.; Peter, Th.; Luo, B. P.; Clegg, S. L.; Carslaw, K. S.; Brimblecombe, P. *J. Atmos. Chem.* **1995**, *81*, 21.

(16) Williams, L. R.; Long, F. S. *J. Phys. Chem.* **1995**, *99*, 3748.

(17) Egsgaard, H.; Carlsen, L. *Int. J. Mass Spectrom. Ion Processes* **1992**, *113*, 233.

(18) Sodeau, J. R.; Horn, A. B.; Banham, S. F.; Koch, T. G. *J. Phys. Chem.* **1995**, *99*, 6258.

(19) Deschamps, J. M. R. *C. R. Hebd. Seances Acad. Sci.* **1957**, *245*, 1432.

(20) Bell, R. P.; Gelles, E. *J. Chem. Soc.* **1951**, 2734. This early thermodynamic calculation is highly uncertain involving many estimated quantities including the solvation free energies ΔG_s for H_2OCl^+ and Cl^-.

The estimate of $\Delta G_s(H_2OCl^+)$ of Bell and Gelles is likely to have an uncertainty on the order of a few tens of kcal mol^{-1}. Note that $\Delta G_s(Cl^-)$ has since been measured (Randles, J. E. B. *Trans. Faraday. Soc.* **1956**, *52*, 1573) to be about 13 kcal mol^{-1} more exothermic than the estimate Bell and Gelles used.

(21) Hammett, L. P.; Deyrup, A. J. *J. Am. Chem. Soc.* **1932**, *54*, 2721.

(22) Rochester, C. H. *Acidity Functions*; Academic Press: New York, 1970.

(23) (a) Liler, M. *Reaction Mechanisms in Sulphuric Acid*; Academic Press: New York, 1971. (b) Bagno, A.; Scorrano, G.; O'Ferrall, R. A. *Rev. Chem. Intermed.* **1987**, *7*, 313.

(24) Cox, R. A.; Yates, K. *J. Am. Chem. Soc.* **1978**, *100*, 3861.

(25) (a) Cox, R. A.; Yates, K. *Can. J. Chem.* **1979**, *57*, 2944. (b) *X* corrected for temperature as in *Ibid*. **1979**, *57*, 2960.

(26) Cox, R. A. *Acc. Chem. Res.* **1987**, *20*, 27.

(27) Taft, R. W. In *Progress in Physical Organic Chemistry*; Taft, R. E., Ed.; John Wiley: New York, 1983; Vol. 14.

(28) Francisco, J. S.; Sander, S. P. *J. Chem. Phys.* **1996**, *102*, 9615.

(29) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17* (Suppl. No. 1).

(30) Gmitro, J. I.; Vermeulen, T. *AIChE J.* **1964**, 10, 740.

(31) Steele, H. M.; Hamill, P. *J. Atmos. Sci.* **1981**, *12*, 517−528.

(32) Massucci, M.; Clegg, S. L.; Brimblecombe, P. *J. Chem. Eng. Data* **1996**, *41*, 765.

(33) Carslaw, K. S.; B. Luo; Peter, Th. *Geophys. Res. Lett.* **1995**, *22*, 1877. The equations developed in this reference for calculating wp H_2SO_4 have a wider range of applicability than that of Table 5 and can also be used to estimate the HNO_3 content of atmospheric sulfuric acid. The wp obtained from Table 5 has a maximum of 1.0 wt % deviation from that obtained from eq 10 of this reference for the range of conditions detailed in Table 5.

(34) Hanson, D. R.; Ravishankara, A. R.; Lovejoy, E. R. *J. Geophys. Res.* **1996**, *101*, 9063.

(35) Hanson, D. R.; *et al. J. Phys. Chem.* **1992**, *96*, 4979.

(36) Press, W. H.; et al. *Numerical Recipes in Pascal*; Cambridge University Press: New York, 1989.

(37) Atkins, P. W. *Physical Chemistry*; W. H. Freeman and Company: San Francisco, 1978; p 867.

(38) Hanson, D. R.; Ravishankara, A. R. *J. Phys. Chem.* **1994**, *98*, 5728. Note that the a_{H_2O} given by this expression are ∼10% different than that of Massucci *et al.*[32] The HCl solubilities obtained using this a_{H_2O} and the expression given in Table 4, however, are consistent with the current measured solubilities. Alternatively, the HCl solubilities of Carslaw *et al.*[14] can be used, which are up to a factor of 2 greater than H^*_{HCl} given in Table 4.