

The hydrolysis of ClONO₂ on sub-micron liquid sulfuric acid aerosol

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Abstract. The reactive uptake of ClONO₂ on liquid sulfuric acid has been measured for size-selected, sub-micron aerosol in the composition range 36–54% H₂SO₄ by weight at ≈ 250 K. A comparison with results from studies employing bulk surfaces at similar temperatures and compositions shows no evidence for a dependence of the reaction probability, γ , on size. We use this observation to estimate an upper limit to the diffuso-reactive length of 26 nm for the ClONO₂ + H₂O reaction on 43 weight % aerosol at 248 K. But, the present values of γ are consistently lower than bulk values observed at lower temperatures and similar composition, suggesting that γ is temperature dependent.

Introduction.

It has been known for a number of years that processing of chlorine reservoir species (ClONO₂ and HCl) on the surfaces of polar stratospheric clouds formed intermittently during the polar winters results in the conversion of these species to photochemically labile compounds which, upon photolysis in spring, release chlorine atoms and precipitate the often rapid ozone destruction observed in these regions [Solomon, 1988; Granier and Brasseur, 1992]. More recently, convincing evidence has been reported that similar reactions occurring on the background liquid stratospheric sulfate aerosol have a significant effect on the chemistry of the global stratosphere, especially during periods of enhanced aerosol loading following volcanic eruptions [Hanson et al., 1994]. One heterogeneous reaction of particular interest is the hydrolysis of chlorine nitrate:



The probability that a gas phase ClONO₂ molecule, on collision with the aerosol surface, is accommodated into the liquid phase and undergoes hydrolysis is denoted by γ . The reaction probability is related to the accommodation coefficient, α (the fraction of collisions that lead to physical accommodation at the liquid aerosol surface), by the following equation:

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{\omega}{4HRT\sqrt{k^l D_l} [\coth(a/l) - (l/a)]} \quad (2)$$

where ω is the mean molecular speed of ClONO₂ in the gas phase, H is the Henry's law coefficient, R is the gas constant, T is

the temperature, k^l is the first order rate coefficient for hydrolysis, D_l is the liquid phase diffusion coefficient, a is the particle radius, and l is the diffuso-reactive length; l is an approximate measure of the distance a ClONO₂ molecule diffuses into the liquid before reaction occurs [Hanson et al., 1994]. Provided that physical uptake is much faster than chemical reaction, *i.e.*, $\alpha \gg \gamma$, as has been shown for ClONO₂ hydrolysis [Hanson, 1998], the value of the reaction probability on bulk surfaces, γ_0 , is related to that on particles of radius a by

$$\gamma = \gamma_0 [\coth(a/l) - (l/a)] \quad (3)$$

Values of γ_0 have been measured over a wide range of composition and temperature using a variety of techniques which have employed bulk liquid surfaces in a Knudsen cell [Williams et al., 1994], on the walls of a flow reactor [Hanson and Ravishankara, 1991 and 1994; Zhang et al., 1994; Hanson, 1998], or as a train of droplets [Robinson et al., 1997]. However, there is only one published measurement of γ for ClONO₂ hydrolysis on liquid sulfuric acid aerosol of a size similar to those found in the atmosphere [Hanson and Lovejoy, 1995].

The purpose of this letter is to report the results of experiments which have extended measurements of the reaction probability for ClONO₂ hydrolysis on sub-micron liquid sulfuric acid aerosol to compositions of lower weight percentage, providing additional data by which to test model treatments of γ . The present results provide a direct comparison with values of γ_0 reported from bulk measurements in order to quantify any effect that the size of the surface may have on the value of γ .

Experimental Method

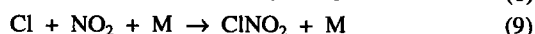
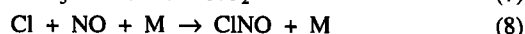
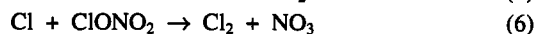
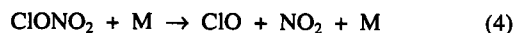
The apparatus used in the present study is a direct adaptation of that used previously to measure the uptake of N₂O₅ on size-selected, sub-micron liquid sulfuric acid aerosol [Fried et al., 1994]. ClONO₂ was reacted with the aerosol in a double jacketed flow reactor, the temperature of which was regulated by circulating ethanol from a thermostatically controlled bath through the inner jacket. The majority of the measurements were performed at a temperature of 248 K and a pressure of approximately 820 mbar. Sulfuric acid aerosol was generated and the particles selected according to their size as before. A flow of ≈ 90 sccm (standard conditions refer to 273 K and 1013 mbar) of scrubbed, dried, "zero" air supplied by an Aadco clean air generator was passed through a trap containing fuming sulfuric acid (18–24% SO₃ by weight) suspended in a temperature controlled water bath. The flow was mixed with a flow of humidified air and admitted into a 94 cm long, 1.7 cm internal diameter stainless steel tube where nucleation of new aerosol particles occurred and where the particles had opportunity to

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grow by coagulation. The ratio of the two flows entering the tube controlled the composition (weight %) of the aerosol. The aerosol flow was passed over a ^{85}Kr source to establish a Boltzmann charge distribution for the differential mobility analyzer (DMA). Particles selected by the DMA lie within a narrow size distribution (half-width about 5% of the mean). The flow of size-selected, monodisperse aerosol was used without neutralization of the particles' charge and formed the major flow in the flow reactor. Flows of 1–2 slpm were employed in the flow reactor.

ClONO_2 was prepared from the reaction of Cl_2O with excess N_2O_5 at $\approx 250\text{ K}$ [Davidson et al., 1987], and the sample was purified by freeze-thaw distillation. A UV absorption spectrum of the purified ClONO_2 sample recorded using a deuterium lamp source and diode array spectrometer showed no evidence of Cl_2 or OClO impurities, or of unreacted Cl_2O or N_2O_5 . During experimental periods, a 1–2 sccm flow of dry N_2 was passed continuously through the trap containing ClONO_2 held at 196 K. The flow was then passed through a shuttered UV absorption cell, and the amount of ClONO_2 entrained into the flow was monitored at the start of each measurement decay. The flow was diluted with "zero" air and admitted into the flow tube via an enclosed movable injector [Henry et al., 1994]. The initial concentration of ClONO_2 in contact with the aerosol was typically 500 parts per billion (ppb) by volume.

The aerosol number density in the gas exiting the flow reactor was measured by drawing off a small fraction of the flow through a TSI model 3760 condensation nucleus counter. As with the N_2O_5 studies [Fried et al., 1994], a tunable diode laser absorption spectrometer (TDLAS) was employed for quantitative measurements of ClONO_2 using a conversion technique with NO as the titrant. The flow reactor effluent was passed through a hot (150°C) quartz converter along with 50 sccm of 22.4 ppm NO in N_2 . The flow reactor effluent plus added NO was directed around the converter using a two-position 4-way valve at the start and end of each decay to measure the initial amount of NO present. In the converter mode, the unreacted ClONO_2 from the flow reactor is thermally decomposed to ClO and NO_2 [Anderson and Fahey, 1990]. Scavenging of ClO radicals by NO resulted in the loss of 1.1 ± 0.1 NO molecules per ClONO_2 molecule independent of the ClONO_2 concentration determined by test experiments in which ClONO_2 samples of known concentration (determined by UV absorption and subsequent dilution) were admitted directly into the converter and the change in the NO signal measured. The key reactions in the converter were



A model of the converter chemistry using the ACUCHEM program [Braun et al., 1988] confirmed the experimentally derived stoichiometry under the range of conditions employed; the experimental value was used in all calculations.

The concentration of NO remaining in the gas flow from the converter was monitored by the TDLAS in a White cell [Fried et al., 1994] using an absorption feature at 1845.5135 cm^{-1} . The concentration of gas phase ClONO_2 remaining in the output flow of the reactor was calculated for different reactant–aerosol contact times from the difference between the measured and initial amounts of NO . An exponential fit to these data yielded a

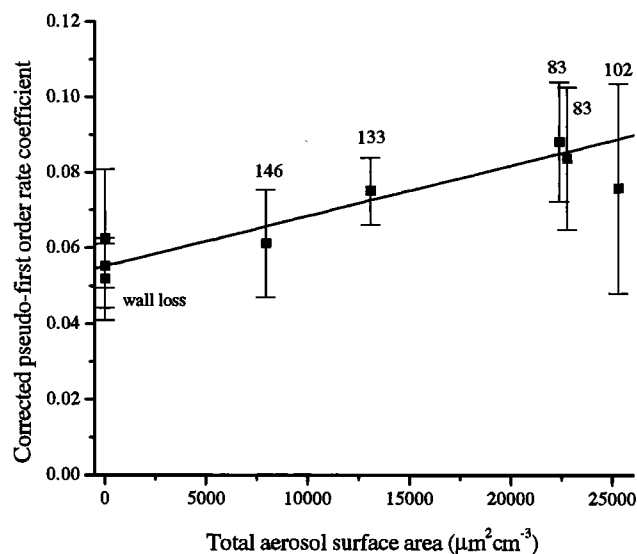


Figure 1. The corrected pseudo-first order loss coefficients for ClONO_2 versus total aerosol surface area at 43.4 weight % and 248 K. The mean particle radius (nm) associated with each measurement is noted on the figure. The line is a linear fit to the data used to determine the value of γ .

pseudo-first order rate coefficient for ClONO_2 loss. Appropriate corrections were made to the rate coefficients for axial and radial diffusion, the presence of double-charged (larger surface area) aerosols [Fried et al., 1994] and mass transport of ClONO_2 from the gas to the liquid phase [Fuchs and Sutugin, 1970]. The experiment was repeated with particles of a different mean radius and number density, and hence total surface area density, selected by the DMA. Values of γ were calculated from the variation of the corrected pseudo-first order rate coefficient with total aerosol surface area and the measured first order rate coefficient for ClONO_2 loss to the reactor's walls. Figure 1 shows an example of such a plot for 43.4 weight % particles. Measurements of γ were confined to relatively wet aerosol where ClONO_2 uptake, and hence the change in NO signal, varied over a reasonable range.

Furthermore, the concentration of water in the flow reactor was monitored contemporaneously via an absorption feature at 1845.2311 cm^{-1} using the technique of jump-scanning [Fried et al., 1993]. The composition of the aerosol at the temperature and relative humidity of the flow reactor was calculated from the measured water concentrations using the equations of Gmitro and Vermeulen [1964] assuming a binary $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solution. However, tertiary $\text{H}_2\text{SO}_4/\text{H}_2\text{O}/\text{HNO}_3$ solutions will form by equilibration of the HNO_3 hydrolysis product between the liquid and gas phases. For example, complete hydrolysis of ClONO_2 in our system would produce ≈ 500 ppb of $\text{HNO}_3(\text{g})$ which in equilibrium with a 42 weight % binary solution at 250 K results in a solution of approximately 36% H_2SO_4 and 6% HNO_3 by weight [Carslaw et al., 1995]. Zhang et al. [1994] found no evidence for a change in γ due to the presence of HNO_3 but Hanson [1998] found an effect for more concentrated solutions of $> 5\%$ HNO_3 (*i.e.*, for solutions of a comparable concentration to those of maximum $[\text{HNO}_3]$ in the present work), although both studies were performed at temperatures substantially below those employed here. Owing to absence of direct evidence for possible effects due to HNO_3 under the present conditions, no attempt has been made to correct the present measurements of γ .

Results

The values of γ for ClONO_2 hydrolysis observed in the present study are presented in Table 1 and Figure 2. The uncertainties quoted are 95% confidence limits of the fit of the pseudo-first order rate coefficient for ClONO_2 loss versus total aerosol area data. Figure 2 also shows values and parameterizations of γ_0 reported by several groups from bulk measurements, and the only other measurement of γ on aerosol particles. The data span a considerable temperature range, 195–253 K, and the present values of γ are in closest agreement with the experimental points of Robinson et al. [1997] and the results of their model at 250 K (open triangles and dot-dash line in Figure 2, respectively), *i.e.*, the present aerosol data agree best with the bulk data recorded at similar temperatures, and are significantly lower than other data taken at lower temperatures.

Several works have sought to resolve variations in γ with temperature and composition into variations in the distinct physico-chemical steps of the uptake, namely, physical solubility (H), liquid phase diffusion (D_l) and reaction (k') [Hanson et al., 1994; Robinson et al., 1997; Hanson, 1998]. The latter two works in particular produced parameterizations of H , D_l and k' , and values of γ calculated from these are in good agreement with the available experimental data over a wide range of conditions. At the temperatures employed in this study (245–253 K), the analysis of Robinson et al. [1997] indicates that H , D_l and k' all decrease with increasing weight %, resulting in a decrease in γ_0 . The parameterizations of H , D_l and k' at 203 K by Hanson [1998] exhibit a similar trend. The analysis of Robinson et al. further indicates that, at a given weight % within the range 36–60%, D_l and k' decrease with decreasing temperature, however, the changes are opposed by a larger increase in H , the net result being that γ is larger at lower temperatures. Comparison of the present data with the other data in Figure 2, which were generally obtained at lower temperatures, further supports the conclusion that γ is temperature dependent.

That the present results are in good agreement with those derived from measurements on bulk surfaces at similar compositions and temperatures is important. Theoretical [Hanson et al., 1994] and experimental results [Hanson and Lovejoy, 1995] have shown that values of γ measured on particles are smaller than those measured on bulk surfaces if the particle radii are similar to or smaller than the diffusive-reactive length, l . In this study, it was assumed that the pseudo-first order loss of ClONO_2 was linearly proportional to the total aerosol area regardless of the mean radius of the size-selected particles, and no deviation from linearity was observed for the small particles (for example, Figure 1). Furthermore, plots at each weight % of the ClONO_2

Table 1. Summary of the measured reaction probabilities and experimental conditions

Temp K	P(H ₂ O) mbar	H ₂ SO ₄ weight %	Radius nm	γ	2σ
245	0.363	36.0	80 to 109	0.071	0.025
248	0.373	42.3	83 to 133	0.037	0.023
249	0.369	42.9	68 to 102	0.047	0.014
248	0.351	43.4	83 to 146	0.031	0.011
248	0.306	45.8	82 to 123	0.025	0.0042
249	0.256	48.9	80 to 141	0.012	0.0058
253	0.279	53.9	50 to 77	0.0094	0.0030

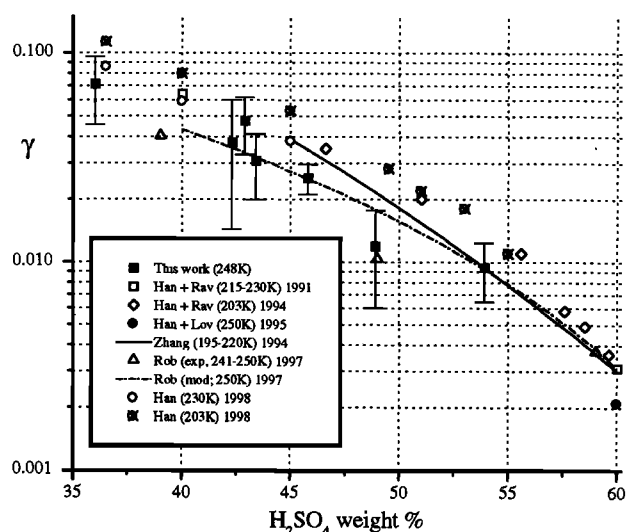


Figure 2. The reaction probability for the hydrolysis of ClONO_2 versus H_2SO_4 weight % from the present aerosol study – solid squares with 2σ error bars. The Hanson and Lovejoy [1995] large particle limit of γ is shown as the solid circle. Other experimental values from bulk liquids are shown as open points and parameterizations of γ_0 are shown as lines.

loss coefficients normalized for the total surface area versus the mean radius showed no decrease in the loss rates on small particles as opposed to what would be expected by analogy to Figure 2 of Hanson and Lovejoy [1995] if the mean radius were close to l : it follows from equation 3 that the value of γ is only some 30% of γ_0 for a particle of radius $a = l$, and such a large difference was not evident in our analysis. Unfortunately, the limited number of data points and their scatter prevented a fit of the form of equation 3 to these data sets in order to extract values for l directly.

Nevertheless, it is possible to estimate an upper limit for l from our data. The average value of γ for the three closely-spaced data points around 43 weight % is 0.038 ± 0.009 , where the uncertainty is twice the standard deviation of the mean. Thus, γ is known to within 25%, and its value, by comparison with the existing data in Figure 2 at the same temperature, is close to that measured on bulk surfaces. A difference of $\leq 25\%$ between γ and γ_0 corresponds to $all \geq 4$ from equation 3, and hence $l \leq 26$ nm assuming $a = 104$ nm (the average of the mean particle radii for these 3 data sets). If the difference between γ and γ_0 were greater, implying in turn that l was larger than 26 nm, our data would have to lie below the bulk data in Figure 2 by an amount at least as large as the uncertainty. Indeed, Figure 1 illustrates that data associated with the smaller particles exert a larger influence on the fits from which the values of γ are derived because the high number concentration of these small particles generated in our apparatus resulted in larger total surface areas, and hence less uncertain ClONO_2 loss rates, than those produced from the lower number concentrations of large particles. Thus, $l = 26$ nm is a conservative estimate of the upper limit because the average particle radius of 104 nm used in its calculation takes no account of the radii of the particles which have the strongest influence on the measured value of γ .

The upper limit of $l = 26$ nm at 43 weight % is significantly smaller than the value of $l = 37 \pm 7$ nm at 60 weight % measured at 250 K by Hanson and Lovejoy [1995]. Although these values

are not directly comparable because they were obtained at different compositions, their ordering is consistent with the model of Robinson et al. [1997] which suggests that l is smaller for more dilute solutions at 250 K within this composition range. However, the model indicates that $l \approx 30$ nm at 40 weight % and 250 K, a value larger than our upper limit. A value approximately half our upper limit, $l = 14$ nm, is obtained at 43 weight % from Hanson's [1998] parameterizations of D_l and k^l at 203 K and the relation $l = \sqrt{(D_l/k^l)}$, a result which also suggests that l is smaller at lower temperatures [Robinson et al., 1997]. Typical background stratospheric sulfate aerosol has a composition of 40–80 weight % H_2SO_4 [Steel and Hamill, 1981] and a mean radius between 150 and 250 nm [Hofmann, 1990] that is almost an order of magnitude larger than any value for l reported above. Thus, we concur with the conclusion of Hanson and Lovejoy [1995] that it is unlikely that the rate of ClONO_2 hydrolysis on stratospheric aerosol is significantly affected by size considerations.

Conclusion

The uptake of ClONO_2 due to hydrolysis has been measured on size-selected, sub-micron liquid sulfuric acid aerosol in the composition range 36–54% H_2SO_4 by weight near 248K. Values of γ obtained in the present study are found to agree (within the experimental uncertainty) with values derived from experiments on bulk surfaces under similar conditions. However, they are consistently smaller than the bulk values reported at lower temperatures, offering supporting evidence that γ depends on temperature within the present composition range. No evidence for a dependence of γ on size was observed, suggesting that the diffusive-reactive parameter, l , for the $\text{ClONO}_2 + \text{H}_2\text{O}$ reaction is substantially smaller than the radii of the particles employed in this study. We estimate an upper limit to l of 26 nm for 43 weight % aerosol at 248 K. Finally, the good agreement between the various experimental and model results provides confidence in extrapolating laboratory results to the atmosphere.

Acknowledgments. We thank Geoff Tyndall for advice on the preparation of ClONO_2 and for his comments on the manuscript, Lee Mauldin also for his comments, John Orlando for assistance with the ACUCHEM modeling and David Hanson for making available to us a copy of his paper prior to its publication. The work was supported by a grant (number 18067) from the NASA's Upper Atmosphere Research Program. NCAR is supported by the National Science Foundation.

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(Received April 8, 1998; accepted July 21, 1998.)