

Mass Accommodation Coefficient for HO₂ Radicals on Aqueous Particles

MICHAEL MOZURKEWICH

National Center for Atmospheric Research, Boulder, Colorado

PETER H. MCMURRY AND ANAND GUPTA

Department of Mechanical Engineering, University of Minnesota, Minneapolis

JACK G. CALVERT

National Center for Atmospheric Research, Boulder, Colorado

The rate of reaction of gas phase HO₂ radicals with a monodisperse, submicrometer aerosol was measured in a flow tube reactor at atmospheric pressure. At the relative humidity of the experiments (75%), the aerosol consisted of concentrated solution droplets of either LiNO₃ or NH₄HSO₄. When the aerosol contained a sufficient amount of Cu(II) ions, reaction of HO₂ with the aerosol was observed. The mass accommodation coefficient for HO₂ on aqueous particles was determined to be greater than 0.2. This implies that in clouds HO₂ mass transport will be limited by gas-phase diffusion and HO₂ will be in equilibrium at the gas-liquid interface. Reactions of HO₂ with Cu(I) and Cu(II) ions in submicrometer aerosols may have a significant role in converting atmospheric odd hydrogen radicals into H₂O₂.

INTRODUCTION

In recent years heterogeneous processes have been recognized as playing an important role in atmospheric chemistry. Of particular interest is the process by which SO₂ is oxidized in forming acid rain; homogeneous gas phase reactions are not sufficiently fast to account for the rate of oxidation observed in the atmosphere [Calvert and Stockwell, 1984]. An understanding of atmospheric heterogeneous chemistry requires a knowledge of the compositions of both the gas and condensed phases, rates of condensed phase reactions, and the rates of mass transfer from the gas phase to the condensed phase. This last rate depends on both the diffusion coefficients and the mass accommodation (sticking) coefficient, α ; this is the fraction of collisions which result in a gas phase molecule entering the liquid. If α is less than about 10⁻², then the rates of processes occurring in cloud droplets become sensitive to this parameter [Chameides and Davis, 1982].

In their modeling calculations, Chameides and Davis [1982] considered a wide range of possible values of α ; very small values appear to be supported by experiments with a variety of atmospheric trace gases on sulphuric acid surfaces [Baldwin and Golden, 1979, 1980; Harker and Ho, 1979], flow tube reactor walls [Martin et al., 1980], and dry salt particles [Jech et al., 1982]. However, values of α near unity are observed for vapors on their own liquids [Pound, 1972; Mozurkewich, 1986] and for NH₃ on liquid H₂SO₄ particles [Huntzicker et al., 1980; McMurry et al., 1983]. We are not aware of any measured values for reactive free radicals on aqueous surfaces.

At this point we must make a distinction between the mass accommodation coefficient, α , and the reaction probability,

γ . The former is the fraction of collisions of a gas molecule with a surface which result in the molecule entering the condensed phase; the latter is the fraction which are permanently trapped or which irreversibly react in the condensed phase. γ is a lower bound to α . It is clear that γ is a strong function of the composition of the particle, the presence of reactive species such as other dissolved gases, and the surface to volume ratio of the particle. On the other hand, α should not depend strongly on these quantities. With a sufficient knowledge of the chemistry and composition of the drop, one may calculate γ if α is known. Experimental accommodation coefficients are actually measurements of γ , in order to apply these results to varying conditions, it is necessary to obtain experimental conditions under which γ approximates α . Quantitative expressions for determining if the rate of gas uptake is limited by mass transport or by solution phase chemistry have been given by Schwartz and Freiberg [1981].

Most interest in the chemistry of heterogeneous atmospheric processes has been centered on the role of clouds. Cloud droplets typically have radii on the order of 10 μ m and consist of dilute aqueous solutions. For such large drops, mass transport will be limited by diffusion unless α is about 10⁻² or less [Fuchs and Sutugin, 1970; Chameides and Davis, 1982]. The drops used in this study have sizes (0.05-0.10 μ m) and ionic strengths typical of the clear air aerosol. Gas phase diffusion is not a significant limitation for particles in this size range, but reevaporation of dissolved species from the drop is much more rapid than for cloud drops.

The experiments described below were designed to measure the mass accommodation coefficient, α , for HO₂ on aqueous aerosol particles. To accomplish this, a flow of gas containing HO₂ was combined with a flow containing a monodisperse, submicrometer aerosol at a relative humidity above the deliquescence point of the aerosol. The decay of HO₂ along the length of the flow tube was measured and the

Copyright 1987 by the American Geophysical Union.

Paper number 7D0085.
0148-0227/87/007D-0085\$05.00

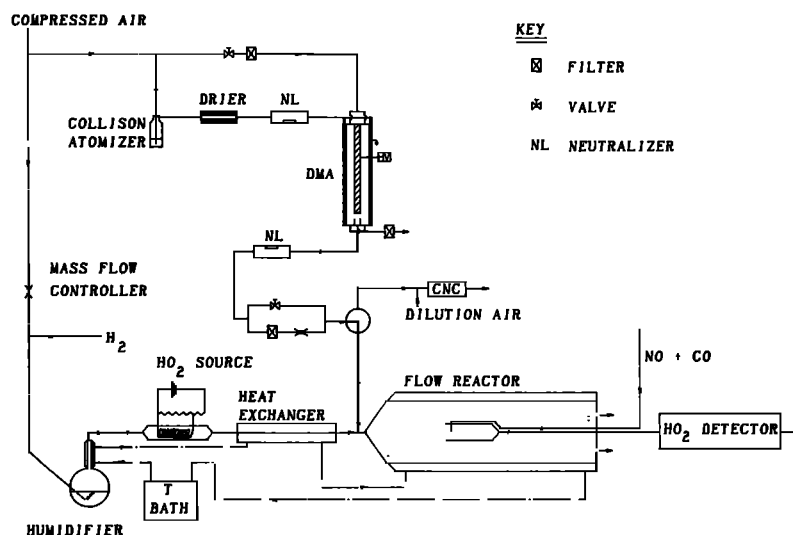
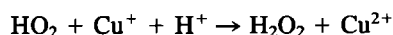
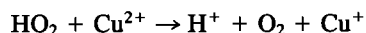


Fig. 1. Schematic diagram of the flow tube and associated equipment.

reaction probability, γ , was calculated. For this to be a measure of α , a sink for HO₂ was provided in the condensed phase, otherwise the aerosol would rapidly come into equilibrium with the gas phase. In these experiments, this was accomplished by adding a Cu(II) salt to the aerosol. Cu(II) catalyzes the condensed phase dismutation of HO₂ via the following sequence [Rabani *et al.*, 1973]:



From the Henry's Law constants for O₂ and H₂O₂ one can show that, for the drop sizes used in these experiments, the products, O₂ and H₂O₂, will rapidly evaporate from the drops.

EXPERIMENT

A schematic diagram of the apparatus used is shown in Figure 1. HO₂ was produced by adding a small amount (0.3%) of H₂ to a flow of air which was saturated with water vapor at 20°C and passed over a coil of hot Nichrome wire. The wire was heated to a dull red glow. It was found that both water vapor and H₂ were needed to produce HO₂ without producing excessive amounts of unwanted organic peroxy radicals (RO₂). The hot wire was also found to produce a substantial number of very small particles with radii of a few nanometers. Number concentrations and size distributions of these particles were measured using the ultrafine aerosol equipment of Stolzenberg and McMurry [1986]. The total surface area of these particles was a factor of 100 less than that of the aerosol which was the object of study; thus, they should have no effect on the results. The flow was partially cooled in a heat exchange prior to being admitted to the flow tube.

As noted above, the hot wire tended to produce both HO₂ and RO₂ radicals. These could be distinguished as follows. When no H₂ or H₂O was added to the flow and no steps were taken to reduce hydrocarbon levels in the air used, the radicals produced were lost slowly to the walls (a factor of ten slower than the diffusion limit) and did not react appreciably with the Cu(II) doped aerosol. Also, under these

conditions, both organic hydroperoxides (ROOH) and H₂O₂ were observed using a fluorometric technique [Kok *et al.*, 1986; Lazrus *et al.*, 1986]. When H₂ and H₂O were added and hydrocarbon levels were reduced (using zero air or treating the air as described below) the radicals were lost rapidly to the walls (approximating the diffusion limit) and reacted readily with the aerosol. Under these conditions, only H₂O₂ and no ROOH was observed. We infer that in the former case RO₂ was being formed and in the latter case HO₂ was obtained. Adding large amounts of aerosol showed that there was always some residual RO₂ that did not react with the aerosol. This residual typically amounted to about 10% at the upstream points to 50% at downstream points. For each decay this was measured and subtracted from all points.

The air used was taken from a compressed air line and purified by passing it over CrO₃ supported on silica gel and then over ascarite to remove NO_x and other acidic gases. The air flow used for the HO₂ source was further purified with a heatless dryer air cleaner (Puregas, model HE204) to reduce hydrocarbon levels. UHP H₂ was used without treatment. The humidifier consisted of a bubbler containing deionized water and followed by a condenser held at the temperature of the experiment.

The aerosol was prepared by using a Collision atomizer to produce a mist from a solution containing the desired salt and then drying the droplets in a diffusion dryer. This polydisperse aerosol was then brought into a Boltzmann charge equilibrium using a Po²¹⁰ radioactive source. The aerosol was next introduced into a differential mobility analyzer (DMA), similar to TSI model 3071. The DMA uses the migration of charged particles in an electric field to select out a monodisperse fraction [Knutson and Whitby, 1975]. The monodisperse aerosol flow was about one std. 1. min.⁻¹ and typically contained 2×10^5 to 3×10^5 particles cm⁻³. For our operating conditions, the size distribution is triangular with essentially all particle radii within $\pm 14\%$ of the mean. The accuracy of the mean radius is better than 10% [Cheng and Denee, 1981]. A small fraction of the aerosol flow was diverted to a diluter [Brockmann *et al.*, 1984] and a single particle condensation nucleus counter (a TSI model 3020 which had been previously modified for ultrafine aero-

sol work, *Stolzenburg and McMurry* [1986]). The remainder was injected into the HO₂ flow through a capillary tube to insure mixing.

The wet particles used in these experiments have radii of 0.05 to 0.1 μm. Use of particles in this size range is convenient since the rate of mass transport is almost entirely gas kinetic and is only slightly affected by diffusion [*Fuchs and Sutugin*, 1970]. Also, for particles of this size the time constants for settling (12 hours) and diffusion to the walls (100 hours) are long enough so that the loss of particles during the experiment is negligible. The use of a monodisperse aerosol makes it easy to determine the surface area from the number concentration and also makes it easy to correct for the small effect of gas phase diffusion, which is size dependent. Since the relative humidity was about 75%, the drops consist of very concentrated salt solutions. At this humidity the drop equilibrates with water vapor in less than a millisecond so that the drops should neither evaporate nor grow during the experiment.

The salt solution used consisted primarily of either LiNO₃ (chosen because of its favorable deliquescence properties and chemical neutrality) or NH₄HSO₄ (which is representative of the atmospheric clear air aerosol, *Charlson et al.* [1978]). To this was added CuSO₄ as a catalyst. Also, the pH of the LiNO₃ aerosol was controlled with either a phosphate (pH7) or phthalate buffer (pH5). All chemicals were reagent grade used without further purification.

The HO₂ and aerosol were combined just before they entered the flow tube through a 3/8" o.d. glass tube. The flow tube was made of Pyrex and was 1.2 m long with an i.d. of 75 mm. Water at a constant temperature of 20°C was circulated through a water jacket. A movable sampling tube, located on the axis of the cell, was used for HO₂ measurements. The relative humidity was determined by measuring the dewpoint of the outflow with a dewpoint hygrometer (EG&G, model 880). From the flow velocity measurements described below it was found to be necessary to place flowsmoothing screens near both the inlet and outlet of the flow tube. The upstream screen and the tubing through which the HO₂ passed were coated with Halocarbon wax in order to reduce losses of HO₂. Uniform mixing of the reactants was verified by measuring the aerosol number density as a function of radial position in the tube.

Since the flow tube was operated at atmospheric pressure, it was not possible to assume plug flow conditions. *Keyser* [1984] has provided a discussion of some of the differences between high pressure flow tubes and the low pressure flow tubes more commonly used in kinetics experiments. If the initial velocity is uniform across the tube, then the distance required to produce a fully developed laminar flow is given by the inlet length [*Goldstein*, 1965]. In our tube, this is about 30 cm. At high pressure, in a sufficiently large tube, the wall loss rate will become independent of the reaction probability at the wall and will approach the diffusion limit [*Gormley and Kennedy*, 1949].

Since the decays of HO₂ are determined by measuring the HO₂ concentration as a function of distance, it is necessary to convert distances into times using a suitable flow velocity. Under laminar flow conditions, both the flow velocity and the HO₂ concentration will be largest near the center of the tube. The appropriate flow velocity for converting distance into time depends on both the velocity and concentration profiles. This problem has been examined in detail by *Walker*

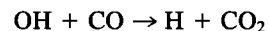
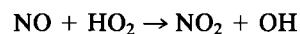
[1961] and by *Brown* [1978]. *Brown* gives plots of numerical results covering a wide range of conditions; for the conditions used here, the appropriate velocity is 60% greater than the mean flow velocity. This result applies to laminar flow; if there was any turbulence in the flow, then the appropriate velocity should be lower since mixing would produce conditions more nearly approximating plug flow.

The assumption of laminar flow was tested by measuring the maximum flow velocity in the tube. By turning the electric field in the DMA on and off we were able to abruptly turn the aerosol on and off without disturbing the flow. Then, using a fast response CN counter [*Stolzenburg and McMurry*, 1986], we measured the time lag for the aerosol concentration change at various points in the flow tube. From this, we determined the maximum flow velocity and compared this to the calculated center line flow velocity for laminar flow. The measured maximum flow velocity was lower than laminar flow by about 20%.

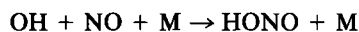
Both the measured maximum flow velocity and the calculated conversion velocity for laminar flow should be upper limits to the appropriate velocity for converting distance to time. These were both 3.4 cm s⁻¹ for our flow tube. The lower bound is the mean velocity of 2.1 cm s⁻¹, as determined from the volumetric flow rate and the tube diameter. For our calculations, we used an intermediate value of 2.75 ± 0.65 cm s⁻¹. The uncertainty is a systematic error and was applied only to the final result and not to intermediate values.

The temperature of the inflowing gasses, measured with a thermocouple, was about 5°C above the wall temperature of the flow tube. By the end of the inlet length of 30 cm the center line temperature was within 0.8°C of the wall temperature. We believe that this small temperature gradient produced some convection in the flow tube and that this convection was responsible for the low value of the maximum flow velocity. For these experiments, the product of the Reynolds and Rayleigh numbers was about 5 × 10⁴, direct experimental measurements of flow velocities [*Mori et al.*, 1966] have shown similar reductions in maximum flow velocity due to similar temperature gradients.

HO₂ measurements were made using the chemical amplifier-luminol detector technique as described by *Cantrell et al.* [1984]. About 2 l min⁻¹ of the flow was drawn into a glass bulb mounted at the end of the sample tube. Here NO and CO were mixed with the flow. This initiates a chain reaction,



which produces as many as 1000 NO₂ molecules before being terminated by the reaction



The NO₂ produced is then detected by means of its chemiluminescent reaction with a luminol solution. Any background due to NO₂ or O₃ in the flow is subtracted out by modulating the CO flow with N₂. We made no attempt to calibrate the detector since only relative concentrations are required in our study. However, based on the work of *Cantrell et al.* [1984], we estimate that the HO₂ concentrations were about 10⁸ to 10⁹ molec cm⁻³. This is sufficiently

low that the gas phase self-reaction of HO₂ should be negligible on the time scale of these experiments (roughly 1 min). In the absence of aerosol the major loss of HO₂ radicals will be at the wall.

RESULTS AND DISCUSSION

As described above, the HO₂ concentration was measured as a function of the downstream distance from the flow tube inlet. The results were fitted to an exponential using weighted least squares. After using the flow velocity to convert distances into times, the results lead to a pseudo-first-order rate constant. This rate constant is the sum of two terms, one from the wall loss and one from the reaction with the aerosol. The wall loss rate was measured in the absence of the aerosol and subtracted out.

The wall loss rate was measured repeatedly during the experiment and was found to be very reproducible. It did not depend on the initial concentration of HO₂, verifying that self-reaction of HO₂ was negligible. However, the wall loss rate did appear to decrease as we increased the downstream distance at which the decay was measured. Also, it was roughly twice as fast as the diffusion limit [Gormley and Kennedy, 1949]. We believe that both of these effects were due to the slight temperature differential between the gas and the walls of the flow tube. This would result in some thermal convection which would enhance the rate of mass transport to the walls. As thermal equilibrium was established downstream, this effect diminished and the wall loss became smaller. Thermal convection has been observed to roughly double rates of heat transfer relative to laminar flow values for similar temperature gradients [Mori *et al.*, 1966]

The average wall loss rate, beginning at the end of the inlet length of 30 cm, was $0.175 \pm 0.007 \text{ s}^{-1}$. This was based on 11 measurements with values ranging between 0.160 ± 0.028 and $0.201 \pm 0.045 \text{ s}^{-1}$. The error bars are twice the standard deviation (2σ) based on the scatter in the data. The scatter about the mean value was consistent with that expected from the estimated uncertainties of the individual measurements. Since the wall loss rate did not change in the course of the experiments, the reactivity of the walls was unaffected by flowing aerosol through the tube. This is consistent with the fact that the number of particles deposited on the walls is negligible.

When aerosol doped with sufficient amounts of Cu(II) was added to the flow, the HO₂ signal decreased and the first-order decay rate increased. All decays were measured beginning at the same point as the wall loss measurements. Sample results without aerosol and with the maximum NH₄HSO₄ aerosol concentration are shown in Figure 2. The pseudo-first order rate constant, k_I , as a function of aerosol concentration is shown in Figures 3 and 4. These results may be expressed as

$$k_I = k_w + k_{II}N \quad (1)$$

where k_w is the wall loss rate constant, k_{II} is the second-order rate constant for reaction with the aerosol, and N is the particle number density. From Figure 3 we see that the second order rate constant appears to be slightly larger when larger particles were used; this is probably due to the greater surface area.

The second-order rate constant, k_{II} , is related to the reaction probability, γ , by the expression [Fuchs and Sutugin, 1970]

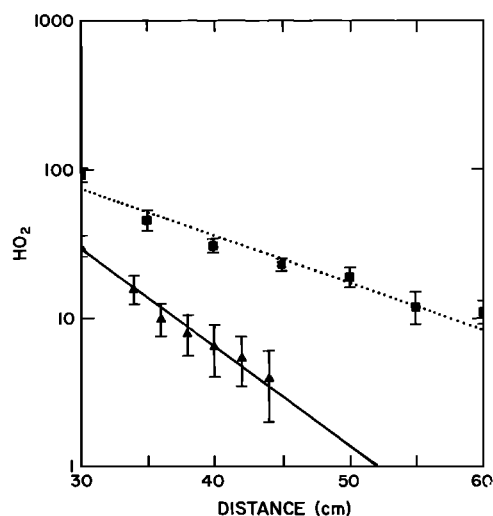


Fig. 2. HO₂ signal as a function of downstream distance with NH₄HSO₄ aerosol ($86,000 \text{ particles cm}^{-3}$, wet radius = $0.055 \mu\text{m}$), triangles, and without aerosol, squares.

$$k_{II} = 4Kn\gamma c\pi a^2 / \{3\gamma + [3\gamma\lambda + 4(1-\gamma)]Kn\} \quad (2)$$

where

$$\lambda = (0.71 + 1.333Kn) / (1 + Kn) \quad (3)$$

The Knudsen number, Kn , is given by

$$Kn = 3D/ca \quad (4)$$

where D is the HO₂ diffusion coefficient in air ($0.247 \text{ cm}^2 \text{ s}^{-1}$, estimated from the value for O₂ and the ratio of the square roots of molecular weights), c is the mean molecular speed for HO₂, and a is the wet drop radius. This equation describes the rate of mass transport in the transition regime between the kinetic theory limit,

$$k_{II} = \gamma c\pi a^2$$

valid when the particle is small compared to the mean free path ($Kn \rightarrow \infty$) and the diffusive limit,

$$k_{II} = 4\pi Da$$

valid for large drops ($Kn \rightarrow 0$). For these experiments $Kn = 1.7$ to 3.4 .

The wet drop radius was calculated from the dry particle radius by using the density of the solution and the equilibrium concentration of the major salt at the relative humidity of the experiment. Small corrections were applied for the Kelvin effect (assuming that the surface tension was the same as for pure water) and the presence of minor salts (CuSO₄ and the buffers) for which an ideal solution was assumed. For NH₄HSO₄, water activity and density data were taken from Tang and Munkelwitz [1977]. For LiNO₃, the dry particle is the crystalline hydrate, LiNO₃ · 3H₂O [Hart and Beumel, 1973]. The density of this salt was taken from Mashovets *et al.* [1969], water activity data were from Robinson [1946], and solution density data were from Meyer [1960]. For both aerosols, the wet particle radius was about 50% larger than the dry radius.

To test these calculations, we made measurements of both the wet and dry particle size using the tandem DMA technique [Rader and McMurry, 1986]. Measured and calculated values agreed within 1% for NH₄SO₄ and 4% for LiNO₃.

The values of γ resulting from the data in Figures 3 and 4

are as follows. For NH₄HSO₄ with a wet particle radius of 0.055 μm, $\gamma=0.53 \pm 0.45$. For NH₄HSO₄ with a wet radius of 0.081 μm, $\gamma=0.34 \pm 0.10$. For LiNO₃ with a wet radius of 0.054 μm, $\gamma=0.57 \pm 0.16$. The error limits are twice the standard deviations.

In addition to the data shown in Figures 3 and 4, a number of other measurements were made with particles of varying size and composition. These data, along with those from the figures, are summarized in Tables 1 and 2. A total of 17 decays were measured with NH₄HSO₄. For each decay, the average wall loss rate was subtracted from the first-order decay rate. This was divided by the particle number density to obtain the second-order rate constant, k_{II} . Then, equation (2) was used to obtain a value of γ ; a weighted average of these yields $\gamma=0.40 \pm 0.08$. The scatter was about twice that expected from the estimated uncertainties of the individual decays. For LiNO₃, a weighted average of 10 decays gave $\gamma=0.94 \pm 0.20$. The scatter was about three times as large as expected. These LiNO₃ values are all larger than those determined from the data of Figure 4. This is because they are based on the average wall loss rate. The wall loss rate obtained from the intercept in Figure 4 is larger than the average.

As was discussed above, measured values of γ are equal to the mass accommodation coefficient, α , only if there is sufficient Cu(II) in the drop to insure that all dissolved HO₂ radicals react before they can reevaporate. Whether the Cu concentration in the aerosols is sufficient can, in principle, be determined from the equations of *Schwartz and Freiberg* [1981] and a knowledge of relevant rate constants and solubilities. However, these parameters have only been measured for relatively low ionic strengths and may be very different at the high ionic strengths encountered in the current experiments. Hence, we have taken an empirical approach to determining if the Cu concentration was sufficient.

In these experiments, we wanted to keep the CuSO₄ concentration as low as possible in order to minimize its effects on the deliquescence properties of the aerosol. On the basis of experiments which showed little effect on the decay rate with differing Cu(II) concentrations, we concluded that the amount of Cu(II) being used was adequate. However, in

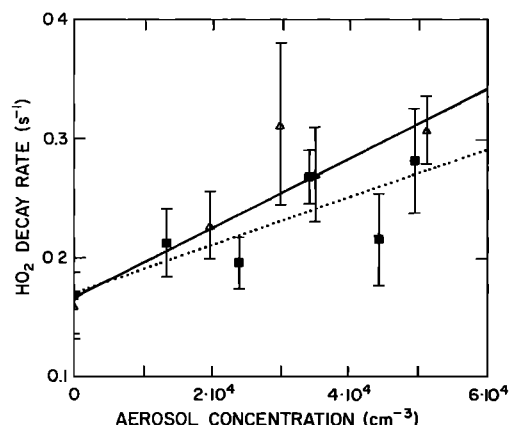


Fig. 3. Aerosol number density dependence of pseudo-first-order rate constants for the decay of HO₂ in the presence of NH₄HSO₄ aerosol. Wet radius of 0.055 microns with 0.06 molal Cu, squares. Wet radius of 0.082 microns with 0.03 molal Cu, triangles.

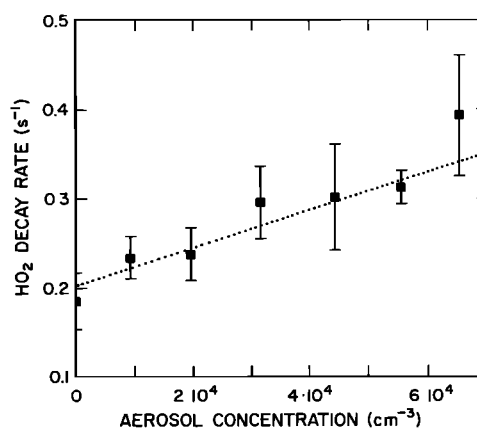


Fig. 4. Aerosol number density dependence of pseudo-first-order rate constants for the decay of HO₂ in the presence of LiNO₃ aerosol with a wet radius of 0.054 microns and a Cu concentration of 0.006 molal.

view of the observed scatter in the data, this conclusion must be questioned.

To resolve this question, we adopted an alternate method of examining the dependence of HO₂ loss on Cu(II) concentration. This consisted of measuring the HO₂ concentration at the 30 cm position in the flow tube as aerosols with increasing concentrations of Cu(II) were added. The ratios of the HO₂ signal with aerosol to that without aerosol are shown as a function of Cu(II) molality in the wet drops in Figure 5. We see from the figure, that, as expected, when only a small amount of Cu(II) is used there is virtually no reaction between the HO₂ and the aerosol. After a fairly sharp transition, the reactivity becomes nearly independent of Cu(II) concentration at large concentrations. Here, the loss rate should be a true measure of the mass accommodation coefficient.

Applying these results to the aerosol compositions used in the above experiments, we find that the concentrations may not have been quite adequate to insure that $\alpha=\gamma$. The data in Figure 5 were obtained at a single point in the flow tube and the flow upstream of this point was not at all well characterized. As a result we cannot quantitatively analyze these data in order to determine exactly how large the error might be.

TABLE 1. Measured Values of the Reaction Probability, γ , for NH₄HSO₄ Aerosols

Wet Radius, μ	Cu(II) Molality	$\gamma \pm 2\sigma$
0.055	0.0059	0.53 ± 0.21
0.081	0.030	0.31 ± 0.08
0.081	0.030	0.32 ± 0.19
0.082	0.029	0.56 ± 0.28
0.082	0.028	0.32 ± 0.13
0.042	0.055	0.61 ± 0.16
0.053	0.065	0.83 ± 0.20
0.078	0.063	0.30 ± 0.13
0.081	0.053	0.29 ± 0.21
0.098	0.067	0.35 ± 0.21
0.101	0.059	0.57 ± 0.37
0.054	0.064	0.58 ± 0.24
0.054	0.064	0.79 ± 0.62
0.054	0.064	0.75 ± 0.20
0.055	0.061	0.78 ± 0.79
0.055	0.058	0.23 ± 0.22
0.055	0.057	0.22 ± 0.24

TABLE 2. Measured Values of the Reaction Probability, γ , for LiNO₃ Aerosols

Wet Radius, μ	Cu(II) Molality	$\gamma \pm 2\sigma$
0.041	0.0031	1.37 ± 0.13
0.054	0.0031	1.53 ± 0.49
0.079	0.0030	0.98 ± 0.15
0.105	0.0030	0.65 ± 0.35
0.053	0.0063	1.10 ± 0.33
0.054	0.0062	0.94 ± 0.30
0.054	0.0062	1.92 ± 0.83
0.054	0.0059	0.67 ± 0.10
0.054	0.0058	0.87 ± 0.43
0.055	0.0056	0.75 ± 0.36

The error would appear to be more severe for LiNO₃ than for NH₄HSO₄; however, γ is already near unity for this system. In any case, the data in Tables 1 and 2 show no apparent dependence of γ on the Cu(II) concentration.

POSSIBLE ATMOSPHERIC IMPLICATIONS

In atmospheric aerosols, HO₂ may react with two classes of species: dissolved trace gases and non-volatile species, such as transition metal ions. For a reaction with HO₂ to be limited by mass transport, the reacting species must be present at a concentration at least comparable to that used in these experiments. Since the rate constant for Cu(II) + HO₂ is only a factor of 10 below the diffusion limit [Rabani *et al.*, 1973], a much lower concentration of reactant cannot be compensated for by a faster rate constant. Even a very soluble gas, such as H₂O₂ or HNO₃, would have to be present at a gas phase mixing ratio of 10 ppb in order to have liquid phase concentrations comparable to the Cu(II) concentrations used in this study. Gases present in the atmosphere at these concentrations are either relatively insoluble or unreactive.

For nonvolatile solutes the situation may be different. In the atmospheric fine aerosol (diameter <3 μ m), typical Cu/S mole ratios are about 2×10^{-3} [Lewis and Macias, 1980; O'Connor and Jaklevic, 1981; Shaw and Paur, 1983; Solomon and Moyers, 1986]. This is roughly one third of the ratio used in this study. Cu constitutes about 0.05% of the

dry mass of the atmospheric aerosol compared to 0.4% for this study. Thus, for the Cu concentrations present in atmospheric aerosols, the reaction rate might approach the mass-transport limit. The most common atmospheric trace metal, iron, is found in fine particles at about 10 times the copper concentration. Since the rate constant for Fe(III) + HO₂ is a factor of 300 slower than for Cu(II) [Bielski *et al.*, 1985], this reaction will be much less important unless ionic strength effects are very large.

The Cu ion catalyzed disproportionation of HO₂ to H₂O₂ and O₂ is potentially significant in the atmosphere. For 10^4 particles cm⁻³ with a typical size distribution [Heikes and Thompson, 1983] and assuming sufficient Cu for $\gamma = 0.5$, the HO₂ lifetime would be about 40 s. This is about the same as the lifetime for gas phase disproportionation at an HO₂ mixing ratio of 100 parts per trillion. This HO₂ concentration is typical of calculated midday concentrations in the eastern United States [Calvert *et al.*, 1985]. Thus, the Cu ion catalyzed reaction might be a major source of atmospheric H₂O₂. Also, under the conditions used by Calvert *et al.*, the HO₂ self reaction is the principal sink for odd hydrogen radicals. Thus, this aerosol reaction may have a significant effect on atmospheric OH and HO₂ concentrations. In contrast to this proposed sink for odd hydrogen radicals, Weschler *et al.* [1986] have suggested that photolysis of Fe(III) complexes in atmospheric particles might be a significant source of odd hydrogen radicals.

The above comments must be considered to be speculative for a number of reasons. There are considerable uncertainties in both the atmospheric Cu concentrations and the condensed phase rate constants. The aerosol copper may not be uniformly distributed among particles, may not be in a soluble form, or may be tied up in unreactive complexes. Furthermore, atmospheric particles may be coated with organic films which may substantially reduce the mass accommodation coefficient [Gill *et al.*, 1983].

CONCLUSIONS

Measured values of the reaction probability of HO₂ with Cu(II) doped aqueous aerosols were 0.94 ± 0.50 for LiNO₃ and 0.40 ± 0.21 for NH₄HSO₄. The uncertainties include both random errors at the 2σ level and a possible systematic error due to uncertainties in the flow conditions and particle radius. The mass accommodation coefficient may be somewhat larger than these values due to the possibility that an inadequate amount of Cu(II) was used. The results may be very conservatively summarized by stating that the mass accommodation coefficient is greater than 0.2 for HO₂ on deliquescent salt particles. It seems reasonable to assume that this is representative of water.

The calculations of Chameides and Davis [1982] and Schwartz [1984] show that the rate of HO₂ uptake by cloud droplets is not strongly affected by the mass accommodation coefficient as long as α is greater than about 0.01. Hence, the application of these results to models of cloud chemistry can be summarized quite simply: at the gas-liquid interface HO₂ will be in equilibrium. For submicrometer aerosols, reactions of HO₂ with Cu ions may be fast enough to be limited by the accommodation coefficient, even if it is large. These reactions may also be important as a sink of odd hydrogen radicals and a source of H₂O₂.

Because of the potential atmospheric importance of these reactions, it is desirable to obtain more accurate values of

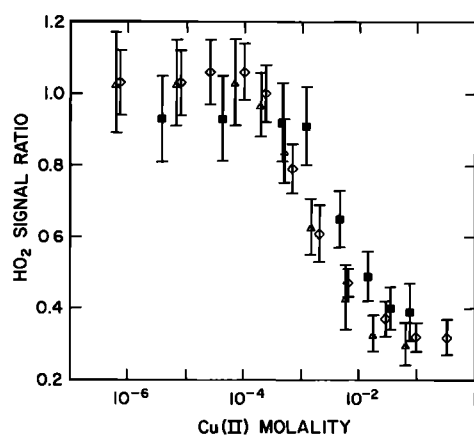


Fig. 5. Ratio of HO₂ signal with aerosol to that without aerosol as a function of the molality of Cu(II) in the wet drop. The measurements were made at the 30 cm position for NH₄HSO₄ (57,000 particles cm⁻³, wet radius = 0.064 μ m), squares, LiNO₃ at pH 7 (58,000 cm⁻³, 0.064 μ m), triangles, and LiNO₃ at pH 5 (52,000 cm⁻³, 0.069 μ m), diamonds.

the accommodation coefficient, and examine more carefully its dependence on ionic media, relative humidity, particle size, and pH. Such studies could yield considerable insight into the solution phase chemistry taking place. To achieve this, an alternate, cleaner HO₂ source, capable of producing higher HO₂ concentrations, is needed. Also, a number of other refinements to the experiment must be made, particularly with regard to the flow properties and Cu concentrations used. We are presently making these improvements with the intent of carrying out further studies.

Acknowledgments. We wish to thank C. A. Cantrell for his assistance with the HO₂ detection equipment, J. A. Lind for his assistance with the peroxide detection, and J. A. Davidson and R. E. Shetter for their assistance with the design and construction of the flow tube reactor. This work was supported by research grants from the National Science Foundation (ATM-851540) and the Environmental Protection Agency (DW49931818-01-0). In addition, M. Mozurkewich was supported by a postdoctoral fellowship from the National Center for Atmospheric Research Advanced Study Program and P. H. McMurry's participation was made possible in part by the University of Minnesota Faculty Single Quarter Leave Program. The National Center for Atmospheric Research is sponsored by the National Science Foundation.

REFERENCES

- Baldwin, A. C., and D. M. Golden, Heterogeneous atmospheric reactions: Sulfuric acid aerosols as tropospheric sinks, *Science*, **206**, 562-563 (1979).
- Baldwin, A. C., and D. M. Golden, Heterogeneous atmospheric reactions, 2, Atom and radical reactions with sulfuric acid, *J. Geophys. Res.*, **85**, 2888-2889, 1980.
- Bielski, B. H. J., D. E. Cabelli, R. L. Arudi, and A. B. Ross, Reactivity of HO₂/O₂⁻ radicals in aqueous solution. *J. Phys. Chem. Ref. Data*, **14**, 1041-1100, 1985.
- Brockmann, J. E., B. Y. H. Liu, and P. H. McMurry, A sample extraction diluter for ultrafine aerosol sampling, *Aerosol Sci Technol.*, **3**, 441-451, 1984.
- Brown, R. L., Tubular flow reactors with first order kinetics, *J. Res. Natl. Bur. Stand.*, **83**, 1-8, 1978.
- Calvert, J. G., and W. R. Stockwell, Mechanism and rates of the gas-phase oxidations of sulfur dioxide and nitrogen oxides in the atmosphere, in *SO₂, NO and NO₂ Oxidation Mechanisms: Atmospheric Considerations*, edited by J. G. Calvert, pp. 1-62, Butterworth, Boston, 1984.
- Calvert, J. G., A. Lazrus, G. L., Kok, B. G. Heikes, J. G. Walega, J. Lind, and C. A. Cantrell, Chemical mechanisms of acid generation in the troposphere, *Nature*, **317**, 27-35, 1985.
- Cantrell, C. A., D. H. Stedman, and G. J. Wendel, Measurement of atmospheric peroxy radicals by chemical amplification, *Anal. Chem.*, **56**, 1496-1502, 1984.
- Chameides, W. L., and D. D. Davis, The free radical chemistry of cloud droplets and its impact upon the composition of rain, *J. Geophys. Res.*, **87**, 4863-4877, 1982.
- Charlson, R. J., D. S. Covert, T. V. Larson, and A. P. Waggoner, Chemical properties of tropospheric sulfur aerosols, *Atmos. Environ.*, **12**, 39-53, 1978.
- Cheng, Y.-S., and P. B. Denee, Physical properties of electrical mobility classified aerosols, *J. Colloid Interface Sci.*, **80**, 284-293, 1981.
- Fuchs, N. A., and A. G. Sutugin, *Highly Dispersed Aerosols*, pp. 47-60, Ann Arbor Science, Ann Arbor, Mich., 1970.
- Gill, P. S., T. E. Graedel, and C. J. Weschler, Organic films on atmospheric aerosol particles, fog droplets, cloud droplets, raindrops, and snowflakes, *Rev. Geophys.*, **21**, 903-920, 1983.
- Goldstein, S., *Modern Developments in Fluid Mechanics*, pp. 299-308, Dover, New York, 1965.
- Gormley, P. G., and M. Kennedy, Diffusion from a stream flowing through a cylindrical tube, *Proc. R. Irish Acad.*, **52**, 163-169, 1949.
- Harker, A. B., and W. W. Ho, Heterogeneous ozone decomposition on sulfuric acid surfaces at stratospheric temperatures, *Atmos. Environ.*, **13**, 1005-1010, 1979.
- Hart, W. A., and O. F. Beumel, Lithium and its compounds, in *Comprehensive Inorganic Chemistry*, edited by A. F. Trotman-Dickenson, p. 360, Pergamon, New York, 1973.
- Heikes, B. G., and A. M. Thompson, Effects of heterogeneous processes on NO₃, HONO, and HNO₃ chemistry in the troposphere, *J. Geophys. Res.*, **88**, 10,883-10,895, 1983.
- Huntzicker, J. J., R. A. Cary, and C.-S. Ling, Neutralization of sulfuric acid aerosol by ammonia, *Environ. Sci. Tech.*, **14**, 819-824, 1980.
- Jech, D. D., P. G. Easley, and B. B. Kreiger, Kinetics of reactions between free radicals and surfaces (aerosols) applicable to atmospheric chemistry, in *Heterogeneous Atmospheric Chemistry*, edited by D. R. Shryer, AGU, Washington, D.C., 1982.
- Keyser, L. F., High-pressure flow kinetics: A study of the OH + HCl reaction from 2 to 100 torr, *J. Phys. Chem.*, **88**, 4750-4758, 1984.
- Knutson, E. O., and K. T. Whitby, Aerosol classification by electric mobility: apparatus, theory, and applications, *J. Aerosol Sci.*, **6**, 443-451, 1975.
- Kok, G. L., K. Thompson, A. L. Lazrus, and S. E. McLaren, Derivatization technique for the determination of peroxides in precipitation, *Anal. Chem.*, **58**, 1192-1194, 1986.
- Lazrus, A. L., G. A. Kok, J. A. Lind, S. N. Gitlin, B. G. Heikes, and R. E. Shetter, Automated fluorometric method for hydrogen peroxide, *Anal. Chem.*, **58**, 594-597, 1986.
- Lewis, C. W., and E. S. Macias, Composition of size-fractionated aerosol in Charleston, West Virginia, *Atmos. Environ.*, **14**, 185-194, 1980.
- Martin, L. R., H. S. Judeikis, and M. Wun, Heterogeneous reactions of Cl and ClO in the stratosphere, *J. Geophys. Res.*, **85**, 5511-5518, 1980.
- Mashovets, V. P., N. M. Baron, and G. E. Zavodnaya, Density of congruently melting hydrates in solid and fused states, *Russ. J. Phys. Chem.*, **43**, 971-974, 1969.
- McMurry, P. H., H. Takano, and G. R. Anderson, Study of the ammonia (gas)-sulfuric acid (aerosol) reaction rate, *Environ. Sci. Technol.*, **17**, 347-352, 1983.
- Meyer, R. J., *Gmelins, Handbuch der Anorganischen Chemie*, vol. 20, p. 290, 1960.
- Mori, Y., K. Futagami, S. Tokuda, and M. Nakamura, Forced convective heat transfer in uniformly heated horizontal tubes, *Int. J. Heat Mass Transfer*, **9**, 453-463, 1966.
- Mozurkewich, M., Aerosol growth and the condensation coefficient of water: A review, *Aerosol Sci. Technol.*, **5**, 223-236, 1986.
- O'Connor, B. H., and J. M. Jaklevic, Characterization of ambient aerosol particulate samples from the St. Louis area by X-ray powder diffractometry, *Atmos. Environ.*, **15**, 1681-1690, 1981.
- Pound, G. M., Selected values of evaporation and condensation coefficients for simple substances, *J. Phys. Chem. Ref. Data*, **1**, 135-146, 1972.
- Rabani, J., D. Klug-Roth, and J. Lilie, Pulse radiolytic investigations of the catalyzed disproportionation of peroxy radicals: Aqueous cupric ions, *J. Phys. Chem.*, **77**, 1169-1175, 1973.
- Rader, D. J., and P. H. McMurry, Application of the tandem differential mobility analyzer to studies of droplet growth and evaporation, *J. Aerosol Sci.*, **17**, 771-788, 1986.
- Robinson, R. A., Osmotic and activity coefficients of lithium nitrate solutions, *J. Am. Chem. Soc.*, **68**, 2402-2403, 1946.
- Schwartz, S. E., Gas- and aqueous-phase chemistry of HO₂ in liquid water clouds, *J. Geophys. Res.*, **89**, 11,589-11,598, 1984.
- Schwartz, S. E., and J. E. Freiberg, Mass-transport limitation to the rate of reaction in liquid droplets: Application to oxidation of SO₂ in aqueous solutions, *Atmos. Environ.*, **15**, 1129-1145, 1981.
- Shaw, R. W., and R. J. Paur, Composition of aerosol particles collected at rural sites in the Ohio river valley, *Atmos. Environ.*, **17**, 2031-2044, 1983.
- Solomon, P. A., and J. L. Moyers, A chemical characterization of wintertime haze in Phoenix, Arizona, *Atmos. Environ.*, **20**, 207-213, 1986.
- Stolzenburg, M. R., and P. H. McMurry, Counting efficiency of an ultrafine aerosol condensation nucleus counter: Theory and experiment, in *Proceedings of the 2nd International Aerosol Conference*, pp. 786-789, Pergamon, New York, 1986.
- Tang, I. N., and H. R. Munkelwitz, Aerosol growth studies, III, Ammonium bisulfate in a moist atmosphere, *J. Aerosol Sci.*, **8**, 321-330, 1977.

Walker, R. E., Chemical reaction and diffusion in a catalytic tubular reactor, *Phys. Fluids*, *4*, 1211–1216, 1961.

Weschler, C. J., M. L. Mandich, and T. E. Graedel, Speciation, photosensitivity, and reactions of transition metal ions in atmospheric droplets, *J. Geophys. Res.*, *91*, 5189–5204, 1986.

J. G. Calvert and M. Mozurkewich, National Center for Atmospheric Research, P.O. Box 3000, Boulder, CO 80307.

A. Gupta and P. H. McMurry, Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455.

(Received September 8, 1986;
revised December 29, 1986;
accepted January 16, 1987.)