JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 88, NO. C15, PAGES 10,721–10,732, DECEMBER 20, 1983

Kinetics and Mechanism of the Oxidation of S(IV) by Ozone in Aqueous Solution With Particular Reference to SO_2 Conversion in Nonurban Tropospheric Clouds

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The kinetics of S(IV) oxidation by ozone in aqueous solution have been studied at 10°C and 25°C in the *p*H range 3.0 to 6.2 by using stopped-flow spectrophotometry. The rate data are empirically correlated by $r = (k_1 + k_2\ 10^{pH})[S(IV)][O_3]$ with $k_1 = 4.39 \times 10^{11}\ e^{-4131/T}$ ($\pm 3 \times 10^4$) $M^{-1}s^{-1}$, and $k_2 = 2.56 \times 10^3\ e^{-966/T}$ (± 15) s^{-1}, at an ionic strength of 0.01 *M*. Reaction rate is unaffected by incident strong UV radiation, or the presence of Mn(II) or Fe(III), but is weakly dependent on ionic strength. The present results, in comparison with reported rates of oxidation of S(IV) by hydrogen peroxide, indicate that at typical *p*H levels encountered in nonurban tropospheric cloud water and at representative concentrations of O_3 and H_2O_2 in the troposphere, oxidation by O_3 can be competitive with that by H_2O_2, or possibly even dominate. The reaction appears to proceed by other than a free-radical process, and a reaction scheme involving direct ozone attack catalyzed by hydroxide ion is proposed. A rate expression consistent with this scheme is $r = (k_a + k_b[OH^-])[HSO_3^-][O_3]$ where $k_a = 3.8 \times 10^5\ M^{-1}s^{-1}$ and $k_b = 1.05 \times 10^{16}\ M^{-2}s^{-1}$ at 25°C. This expression correlates the present data with literature data over the *p*H range 1.0 to 6.2.

1. INTRODUCTION

Sulfur dioxide in the atmosphere can be converted to sulfate aerosol by one or more of several pathways. Of these, oxidation within the aqueous droplet phase of tropospheric clouds has been identified as a major contributor [*Möller*, 1980]. There is a growing general acceptance that much of this droplet-phase oxidation is by hydrogen peroxide [*Penkett et al.*, 1979; *Middleton et al.*, 1980; *Möller*, 1980], with the contribution from ozone being only minimal. Although available kinetic data support this conclusion at cloud water *p*H levels below about 4.5, the case at higher *p*H's is not so clear, in view of the wide disparity in S(IV) oxidation rates reported for O_3 [*Erickson et al.*, 1977; *Larson et al.*, 1978; *Penkett et al.*, 1979]. Since *p*H levels measured in nonurban tropospheric clouds typically lie above 4.5 [*Hegg and Hobbs*, 1981], there is a need to reexamine the kinetics of ozone oxidation at these higher *p*H levels.

The present paper presents the results of a laboratory study of the kinetics of the S(IV)-O_3 reaction in aqueous solution, including measurements of the effects of UV radiation, dissolved transition metals, and an antioxidant (hydroquinone) on the rate. Based on the results obtained, relative rates of S(IV) conversion by O_3 in tropospheric cloud water are compared with those predicted for H_2O_2 and also O_2. Reaction mechanism is discussed, and the elements of a possible reaction scheme are outlined.

2. EXPERIMENTAL

2.1. Kinetic Measurements

Measurements of the rate of the S(IV)-O_3 reaction in aqueous solution were made by using a stopped-flow spectrophotometric technique similar to that used by *Penkett et al.* [1979] and by *Erickson et al.* [1977]. The rate of conversion of S(IV) to sulfate was followed by the loss of ozone monitored by UV absorption at 260 nm (instrument wavelength resolution 3.5 nm). Calibration for the molar absorptivity of O_3 in solution gave $\varepsilon_{260} = 3025\ M^{-1}\ cm^{-1}$. This value compares favorably with the 2930 $M^{-1}\ cm^{-1}$ determined by *Kilpatrick et al.* [1956], the 2900 $M^{-1}\ cm^{-1}$ determined by *Hoigné and Bader* [1976], the 3000 $M^{-1}\ cm^{-1}$ used by *Penkett et al.* [1979], and the $\varepsilon_{260} \simeq 3000\ M^{-1}\ cm^{-1}$ (based on $\varepsilon_{250} = 2430\ M^{-1}\ cm^{-1}$ and $\varepsilon_{276} = 2150\ M^{-1}\ cm^{-1}$) used by *Erickson et al.* [1977]. Mixing dead time of the stopped-flow apparatus was determined to be about 2 ms. Kinetic experiments were conducted at both 10°C and 25°C. Chemicals used were certified grade purity and were used without further purification. Buffer solutions of the desired *p*H, buffering capacity, and ionic strength were prepared by using filtered, deionized water (18-mΩ resistivity) deoxygenated by sweeping with N_2, to which was added the desired quantity of HCl, H_2SO_4, phosphate buffer salts, citric acid, NaOH, NaCl, or Na_2SO_4. The O_3 and S(IV) reactant solutions were prepared from a *p*H buffer solution by bubbling nitrogen-diluted ozonized oxygen from a silent discharge ozonizer through one portion and by dissolving a measured quantity of Na_2SO_3 into another portion. Without delay the reactant solutions were charged into the stopped-flow spectrophotometer, and the initial O_3 concentration was determined by UV absorption of the pure-O_3 buffer solution. Several successive rate measurements were then made, storing the UV absorption decay traces in a calculating digital storage oscilloscope. Immediately following the rate measurements, the S(IV) reactant solution was analyzed for total S(IV) by titration with KIO_3 in acid KI solution. The rate constant for a kinetic run was determined by using an average absorption decay trace obtained by averaging the first three sequential stored decay traces that showed repetition.

2.2. Photoexcitation Studies

To determine the effect of broad-spectrum UV radiation on reaction rate, the stopped-flow spectrophotometer was modified by focusing the output from a 75-W xenon arc lamp through the observation cell in the spectrophotometer in place of the 260-nm monochromatic light beam. As before, rate data were acquired by monitoring ozone decay at 260 nm, but they were obtained in these studies by interposition of a 260-nm interference filter (8.5-nm half-bandwidth, 19% transmission)

Paper number 3C0416.

either between the observation cell and the photomultiplier detector or between the xenon lamp and the observation cell. (A rough indication of the intensity of the xenon lamp was obtained by comparing the photomultiplier signal when viewing the lamp through the filter and observation cell with that when similarly viewing the sun. For a clear day in early March in Hampton, Virginia, this comparison gave a relative intensity of the xenon lamp 16 times that of the noonday sun.)

2.3. Catalysis Studies

Solutions 2×10^{-5} M in Mn(II), Fe(III), or both were prepared from reagent grade $MnCl_2 \cdot 4H_2O$ or $FeCl_3 \cdot 6H_2O$ by dissolving them in the desired aqueous buffer solution at the approximate final pH and ionic strength desired. These metal ion solutions were deoxygenated by sweeping them with N_2 for $1\frac{1}{2}$ to 2 hours prior to dissolving the desired quantity of Na_2SO_3 under anaerobic conditions. Solution pH was then adjusted, as necessary, by adding H_2SO_4. To avoid unwanted oxidations, ozone reactant solutions were prepared in the usual manner in the absence of the metal salts. (Separate rate measurements were made in the stopped-flow spectrophotometer to verify that any metal-ion reactions with O_3 were too slow to interfere with measurements of the S(IV)-O_3 reaction rate.) All Fe(III) reactant solutions were light yellowish in color because of the presence of insoluble colloidal ferric hydroxides.

2.4. Inhibition Studies

Prior to studying the effect of hydroquinone (HQ) on the rate of the S(IV)-O_3 reaction, the kinetics of the HQ-O_3 reaction had to be determined. Since aqueous solutions of HQ absorb in the UV at all wavelengths up to about 320 nm, ozone depletion cannot be conveniently monitored at 260 nm, especially since absorption at 260 nm increases as HQ is oxidized. From UV spectral scans of different concentrations of HQ in solution before and after reaction with ozone, little change in absorbence was observed in the wavelength region 270 nm to 276 nm for HQ in excess. Detailed examination of absorbance changes in this wavelength region in the stopped-flow spectrophotometer revealed the molar absorbtivity of the HQ oxidation product at 272 nm to be the same as that of unreacted HQ. Since at 272 nm, ozone still has a relatively large molar absorptivity (determined to be about 2500 M^{-1} cm^{-1}), ozone consumption in the presence of HQ can be followed at this wavelength. In further studies the stoichiometry of the HQ-O_3 reaction was determined to be between $2\frac{1}{2}$ to 3 moles of O_3 per mole of HQ, which compares favorably with the 3 moles of ozone required for the ozonation of benzene and its homologs [*Bailey*, 1977] and the 3 moles generally required for many organic solutes [*Hoigné and Bader*, 1978]. Studies of the kinetics of ozonation of HQ, and of S(IV) in the presence of HQ, were conducted in the usual manner, but with ozone consumption followed at 272 nm.

3. Results and Discussion

3.1. Experimental Results

The rate data obtained were found to conform well to the second-order rate expression

$$r = -\frac{d[O_3]}{dt} = k[S(IV)][O_3] \qquad (1)$$

This agrees with the experimental observations of *Erickson et al.* [1977], *Larson et al.* [1978], *Penkett et al.* [1979], and *Martin and Damschen* [1982], although at pH's below 4, Penkett et al. found the reaction order with respect to S(IV) to increase somewhat. The possibility of photoexcitation of the reaction by the monitoring, monochromatic UV light beam was ruled out in the present study by several experiments in which the monitoring light intensity at 260 nm was decreased by 1 and 2 orders of magnitude by interposition of neutral density filters. No effect on reaction rate was observed.

In kinetic experiments at pH 5.3 or below, pseudo first-order conditions were usually maintained by employing initial S(IV) concentrations 3 to 10 times the initial O_3 concentrations. Typically, initial S(IV) concentrations ranged from 10^{-5} M to 10^{-4} M. For these conditions, first-order kinetics with respect to O_3 are indicated by the linear decrease of ln(absorbance) as a function of time, as shown by the sample plot in Figure 1. (Time is measured from that point when absorbance noise resulting from mixing was no longer evident.) The second-order rate constant was calculated from the pseudo first-order rate constant by using a value for [S(IV)] adjusted for its partial consumption by using 1 : 1 stoichiometry (*Espenson and Taube* [1965], and verified in the present study). First-order kinetics in S(IV) were demonstrated in several experiments by reducing the initial concentration of [S(IV)] by about one half while still maintaining pseudo first-order conditions. This reduction in [S(IV)] produced no effect on the second-order rate constant.

Above pH 5.3, the reaction generally proceeded too fast to observe accurately under pseudo first-order conditions, and smaller, more nearly equal, reactant concentrations were employed. Typically, initial S(IV) concentrations were on the order of 10^{-5} M. For these conditions, and for certain other cases below pH 5.3, as appropriate, rate constants were obtained from the absorbence data by using the integrated form of (1) with 1 : 1 stoichiometry. A sample plot of kt as a function of time is shown in Figure 2, where overall second-order kinetic behavior is demonstrated by the linearity of the plot. Calculated values of k were the same, whether obtained under pseudo first-order or overall second-order experimental conditions. Details of the experimental conditions are given in Table 1. Because of the speed of the reaction, it was not possible to select a set of experimental conditions that permitted accurate rate measurements above pH 6.2.

The second-order rate constants derived from the data are plotted in Figure 3 as a function of pH for 10°C and 25°C, for a constant ionic strength of 0.01 M. The different buffer systems, indicated by the different symbols in Figure 3, have no clear effect on the reaction rate. Solution ionic strength does, however, have a measurable, although relatively small, effect. This is illustrated in Figure 4, where log k from three separate studies of the effect of ionic strength I is plotted as a function of

$$\frac{I^{1/2}}{1 + I^{1/2}} - 0.3\ I$$

(Selection of these particular coordinates is discussed in the Appendix.) Figure 4 correlates the rate constants reasonably well as a function of ionic strength up to as high as 0.94 M. From this plot the maximum reaction rate expected at high ionic strengths is likely to be less than twice that at very low ionic strength. Also, an estimate of the reaction rate constant at infinite dilution can be obtained from this figure. The significance of the slopes in Figure 4 is discussed in the Appendix and in section 4.

The rate constants in Figure 3 are fit well by the empirical correlation (at $I = 0.01$ M)

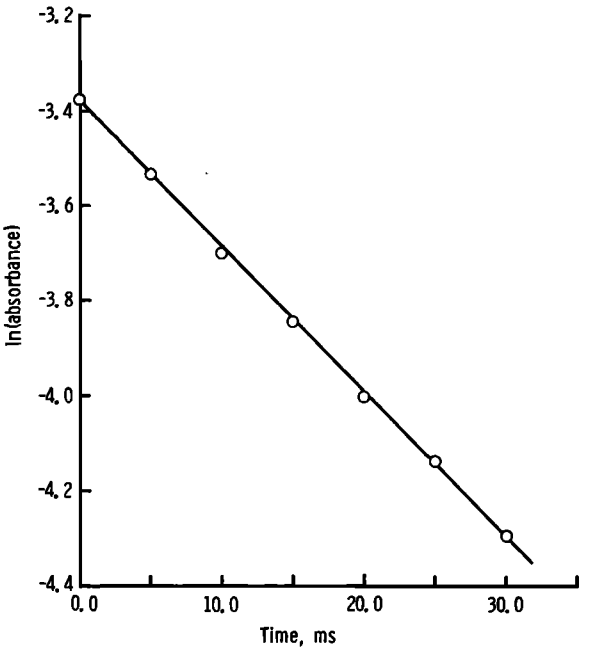


Fig. 1. Linear decay of ln (absorbence) for ozone. Initial mixture $[O_3] = 1.49 \times 10^{-5}$ M and initial mixture [S(IV)] = 1.05×10^{-4} M, at pH 3.0, 10°C, citrate buffer, ionic strength 0.01 M.

$$k = k_1 + k_2 10^{pH} \tag{2}$$

with $k_1 = 4.39 \times 10^{11}\ e^{-4131/T} M^{-1}\ s^{-1}$ and $k_2 = 2.56 \times 10^3\ e^{-966/T}\ s^{-1}$. To obtain these values, the data in Figure 3 for 10°C and 25°C were each fit separately by least squares, and the temperature dependencies of k_1 and k_2 were determined on the results. Error bounds are $\pm 3 \times 10^4\ M^{-1}\ s^{-1}$ and $\pm 15\ s^{-1}$ for k_1 and k_2, respectively, and ± 920 K and ± 1300 K, respectively, for the temperature dependencies of k_1 and k_2. The curves in Figure 3 were plotted by using (2).

3.2. *Comparison with Literature Data*

In Figure 5 the present results are compared with literature data for the oxidation of S(IV) by both O_3 and H_2O_2 at 25°C. For this comparison the data are plotted as specific reaction rate $k[Ox] = r/[S(IV)]$, where $[Ox] = [O_3]$ or $[H_2O_2]$. As discussed later, $[O_3]$ in cloud water is taken to be 5×10^{-10} M, and $[H_2O_2]$ is taken to lie between 4.3×10^{-6} M and 4.3×10^{-5} M. The solid lines indicate the pH range over which supporting experimental data exist, and the dashed lines represent extrapolation. Best agreement of the present data is clearly with the extrapolated results of *Erickson et al.* [1977], plotted using their rate expression

$$r = (k_{SO_2}[SO_2 \cdot aq] + k_{HSO_3^-}[HSO_3^-] + k_{SO_3^{-2}}[SO_3^{-2}])[O_3] \tag{3}$$

where $k_{SO_2} \ll k_{HSO_3^-}$, $k_{HSO_3^-} = 3.1 \times 10^5\ M^{-1}\ s^{-1}$, and $k_{SO_3^{-2}} = 2.2 \times 10^9\ M^{-1}\ s^{-1}$. This rate expression implies that O_3 reacts with SO_3^{-2} more than 7000 times faster than it does with HSO_3^-. The roughly first-order dependence on pH above about pH 4 is due to the domination of the second term at these pH values and the fact that $[SO_3^{-2}]$ varies roughly as $[S(IV)]/[H^+]$.

In Figure 5 the curve shown for *Penkett et al.* [1979] over the pH range 1–5 is based on rate constants from their Table 2, while that over the range 4–7 is based on rate constants from their Table 6, after adjustment to 25°C (from 10°C) by using activation energies reported in their paper. These higher pH 'results' are not experimental but merely represent a straight-line extrapolation by Penkett et al. of their experimental data at lower pH's. In addition, Penkett et al.'s experimentally measured rates at pH 5 have to be low because their reactant solutions were not buffered. This neglect of buffering produces a reaction environment in which the solution pH decreases as the reaction proceeds, thereby slowing its rate. At pH 5, where their initial $[O_3]$ was twice their initial $[H^+]$, their experimentally observed rate must be considerably slower than the true rate if the pH has been held constant.

The very low, virtually pH-independent rate curve shown for *Larson et al.* [1978] is plotted from their rate expression

$$r = kK_H P_{O_3}[HSO_3^-][H^+]^{-0.1} \tag{4}$$

where $k = 4.4 \times 10^4\ M^{-0.9}\ s^{-1}$ and $K_H = 0.0123\ M\ atm^{-1}$ at 25°C, for $P_{O_3} = 50$ ppb. In their study, a stream of low-concentration gaseous O_3 (below ppm) was bubbled through an S(IV) solution in a reaction vessel, and samples were withdrawn periodically for analysis of unreacted S(IV) by *West and Gaeke* [1956] colorimetry. Aqueous phase $[O_3]$ was not measured but was assumed to be in Henry's Law equilibrium with gas-phase O_3. Whereas the low gas-phase concentrations of O_3 that were employed afforded reaction rates sufficiently slow to permit analysis for consumed S(IV) on the withdrawn samples, at the same time they gave rise to the possibility [*Larson*, 1980] that some of the O_3 was consumed in reacting with trace-metal impurities in the solution. If so, this could easily account for the observed low reaction rates. Other possible explanations for the low rates include lack of attainment of ozone gas-liquid equilibrium during bubbling and reaction [*Schwartz*, 1983], interferences in their analytical method, or a real concentration effect from low ozone concentrations. Regarding their analytical method, it has been noted that West-Gaeke colorimetry is subject to a variety of influences and also suffers from a lack of reproducibility and reliability, with analyses for S(IV) in the

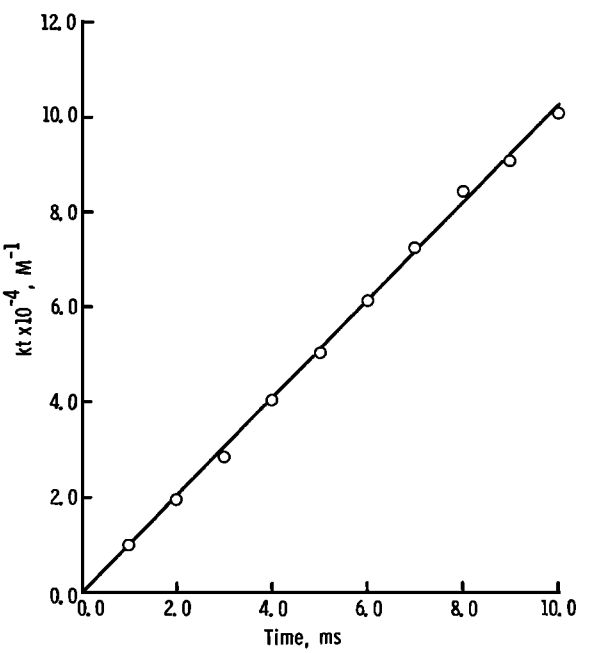


Fig. 2. Plot of kt as a function of time. Initial mixture $[O_3] = 1.19 \times 10^{-5}$ M and initial mixture [S(IV)] = 2.63×10^{-5} M, at pH 5.0, 10°C, citrate buffer, ionic strength 0.01 M.

TABLE 1. Experimental Conditions

pH	Temperature °C	Buffer System*	Ionic Strength, M	Initial Concentration of Mixed Reactants: $[O_3]_0 \times 10^5$, M	Initial Concentration of Mixed Reactants: $[S(IV)] \times 10^5$, M	Number of Runs
3.0	10	citrate	0.01	1.2–1.5	5.3–10.5	2
3.1	10	HCl	0.01	1.6–8.5	9.4–9.5	3
3.1	10	H_2SO_4	0.01	0.56–1.4	2.7–10.4	5
3.1	25	HCl	0.0013–0.10	0.81–1.8	6.5–11.0	12
4.0	10	citrate	0.01	1.1–1.8	9.6–10.0	2
4.0	25	HCl	0.0003	0.89–1.2	7.0	3
4.0	25	citrate	0.01	0.93–1.4	9.1–9.6	5
4.6	25	citrate	0.01	0.89–1.3	9.8–9.9	3
5.0	10	citrate	0.01–0.94	0.91–1.2	1.1–5.4	14
5.1	10	citrate	0.01	1.1–1.3	9.9–10.0	3
5.1	25	citrate	0.01–0.10	1.4–1.6	7.8–10.0	8
5.3	10	phosphate	0.01	1.0–1.8	1.0–10.2	4
5.3	25	phosphate	0.01–0.10	0.71	7.4	1
5.8	10	phosphate	0.01	0.53–0.70	1.0	3
5.8	25	phosphate	0.005–0.01	0.58–0.73	0.83–2.2	3
6.2	10	phosphate	0.01	1.1–1.7	0.98–1.0	2
6.2	10	citrate	0.01	0.52–0.70	1.0	2
6.2	25	phosphate	0.005–0.01	0.46–0.61	0.86–0.99	5

*HCl or H_2SO_4 designates concentration buffering only; citrate designates a citric acid–sodium citrate system; phosphate designates a mixed acid phosphate system.

presence of O_3 giving erratic nonstoichiometric results [*Scaringelli et al.*, 1967]. Another area of concern is whether the fritted glass plate for ozone dispersion in their reaction vessel may be either decomposing the ozone or catalyzing unwanted side reactions, as has been observed in some ozonations employing fritted bubblers [*Perrich et al.*, 1977; *Parry and Hern*, 1973].

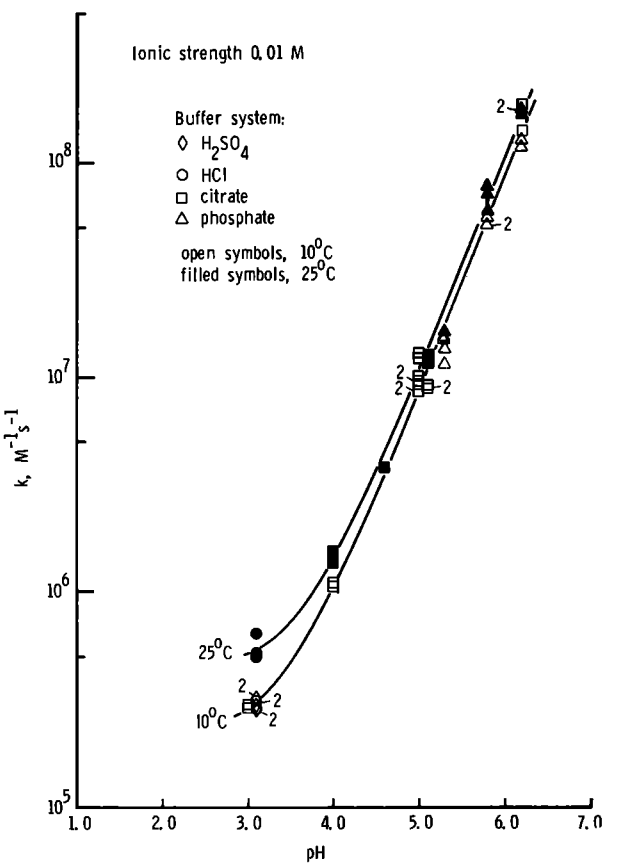


Fig. 3. Second-order reaction rate constant.

Not shown in Figure 5 are the recent results of *Martin and Damschen* [1982] in the pH range 0 to 3 that are virtually coincident with the curves shown for Erickson et al. and Penkett et al. in this range. They give for their rate expression

$$r = k([SO_2 \cdot aq] + [HSO_3^-])[O_3]/[H^+]^{1/2} \quad (5)$$

where $k = 1.9 \times 10^4\ M^{-1}\ s^{-1}$ at 25°C.

3.3. UV Radiation

The rate constants in Figure 3 were obtained under conditions of incident monochromatic light where photoexcitation was demonstrated to be negligible. But since cloud droplets are exposed to full-spectrum solar radiation, it was of interest to determine whether more intense, incident, full-spectrum UV radiation affects the measured rate constants. To examine this possibility, rate studies were conducted while the reactants were exposed to radiation from a 75-W xenon arc lamp. Comparative measurements were made in which a 260-nm interference filter was placed first between the lamp and the observation cell and then between the observation cell and the photomultiplier. No difference in rate was observed. Further, rate constants measured when the reactants were exposed directly to the xenon source (see Table 2) agree well with those plotted in Figure 3. That sufficient energy was available from the xenon lamp to initiate a rate change in a photosensitive reaction was verified in separate experiments of ozone self-decomposition. When exposed to the xenon lamp, ozone solutions decayed roughly 13 times faster at pH 3 and 19 times faster at pH 5 than under dark conditions (i.e., when exposed only to monochromatic light). Hence, whereas ozone self-decomposition is photocatalyzed (likely by catalyzing its reaction with H_2O or OH^- [*Kilpatrick et al.*, 1956; *Ivanov et al.*, 1972; *Peleg*, 1976]), the rate of the S(IV)-O_3 reaction does not depend on this decomposition. (It may be noted that S(IV) ozonation proceeds at a rate many orders of magnitude faster than ozone self-decomposition.) As a result of these experiments it is considered likely that the rate of S(IV) ozonation within cloud droplets is independent of solar intensity. This is not to say, of course, that photochemical production of ozone in the gas phase is not

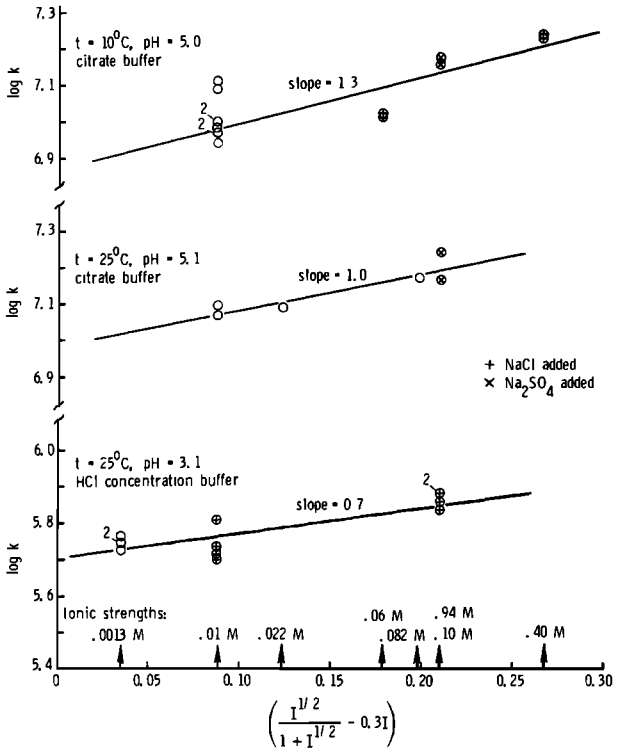


Fig. 4. Effect of solution ionic strength on the second-order reaction rate constant.

enhanced by solar radiation nor that any increase in gas-phase ozone thus produced is not available for dissolution in cloud droplets.

3.4. Transition Metals

A number of transition metals occur naturally within atmospheric aerosols. Because of their relative abundance and their demonstrated effectiveness for catalyzing the autoxidation of S(IV) in solution, Mn(II) and Fe(III) are particularly likely candidates for catalyzing the air oxidation of S(IV) within cloud droplets [*Hegg and Hobbs*, 1978; *Beilke and Gravenhorst*, 1978; *Graedel and Weschler*, 1981]. Therefore, it was of interest to investigate the catalytic effect of these metals on the S(IV)-O_3 reaction. As noted by Graedel and Weschler, Mn(II) is likely to function as a homogeneous catalyst because of its high solubility in even only slightly acid solution, whereas Fe(III) is more likely to function as a heterogeneous catalyst (as ferric hydroxides) because of its low solubility.

Rate constants were measured in the presence of either Mn(II), Fe(III), or both, at 10°C and $I = 0.01$ M over the *p*H range 3.0 to 5.5. Experimental conditions and kinetic results are given in Table 3. Experiments were conducted in unbuffered as well as in buffered solutions to eliminate uncertainties regarding metal complex formation with the buffer or with S(IV) caused by the buffer. In the buffered solutions the rate constants obtained are identical to those plotted in Figure 3. For the unbuffered solutions where meaningful rate constants cannot be derived because of the *p*H decrease during reaction, the extent of catalytic behavior was assessed by comparing the ozone consumption rates with those for identical reactant solutions, except without metal ion added. No catalysis was evident at any of the conditions investigated. Since synergism sometimes has been reported in the catalysis of S(IV) autoxidation by Mn(II) + Fe(III) [*Hoather and Goodeve*, 1934; *Barrie and Georgii*, 1976; *Martin and Damschen*, 1982], one experiment was conducted with both metals present. No catalysis was observed.

TABLE 2. Rate Constants Obtained in Ultraviolet Radiation Experiments at 10°C and Ionic Strength 0.01 M

*p*H	Buffer System	$[O_3]_0$, M	$[S(IV)]_0$, M	k, $M^{-1}\,s^{-1}$
3.0	H_2SO_4*	9.5×10^{-6}	1.1×10^{-4}	2.91×10^{5}
3.0	H_2SO_4*	1.5×10^{-5}	1.1×10^{-4}	2.96×10^{5}
5.0	citrate	8.1×10^{-6}	5.4×10^{-5}	7.61×10^{6}
5.0	citrate	7.5×10^{-6}	2.7×10^{-5}	9.08×10^{6}

*Concentration buffered.

The lack of catalysis observed in the present study is in agreement with the recent findings of *Martin and Damschen* [1982], who report a similar lack of catalysis by metal ions in the lower *p*H range 0 to 3. Both these results conflict, however, with the findings of Barrie, quoted by *Barrie and Georgii* [1976], and the recent results of *Harrison et al.* [1982]. Barrie reports that 10^{-5} M Mn(II) in a droplet doubles the rate of SO_2 absorption from an SO_2-O_3-air atmosphere as compared with that for distilled water, the Mn(II) presumably catalyzing the SO_2-O_3 reaction. Details, however, are sketchy, and it is difficult to assess the significance of this result. Harrison et al. find a complicated catalytic behavior for both Mn(II) and Fe(III). At *p*H 4.5, and a catalyst concentration of 10^{-5} M, they observe a fivefold rate increase caused by Mn(II) and a twofold increase for Fe(III), with these increases falling off rapidly at both higher and lower *p*H's. Under certain conditions, inhibition was even

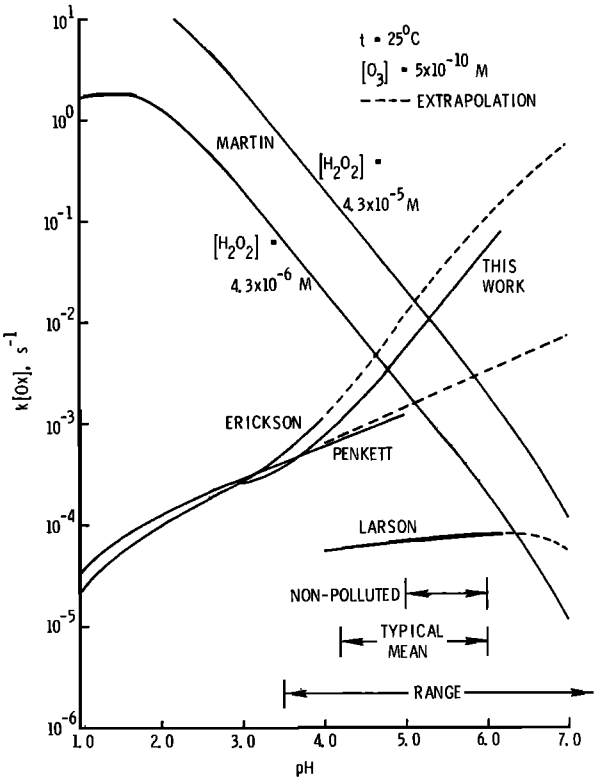


Fig. 5. Specific reaction rate, $k[Ox] = r/[S(IV)]$ as a function of solution *p*H at 25°C. Experimental data for ozone are compared with results from *Erickson et al.* [1977], *Larson et al.* [1978], and *Penkett et al.* [1979] for $[Ox] = [O_3] = 5 \times 10^{-10}$ M, and with results from *Martin et al.* [1981] for $[Ox] = [H_2O_2] = 4.3 \times 10^{-5}$ M and 4.3×10^{-6} M. The *p*H range, typical mean *p*H values, and typical nonpolluted *p*H levels reported in tropospheric cloud water are indicated.

TABLE 3. Rate Constants Obtained in Transition Metal Experiments at 10°C and Ionic Strength 0.01 *M*

*p*H	Buffer System	$[O_3]_0$, *M*	$[S(IV)]_0$, *M*	[Mn(II)], *M*	[Fe(III)], *M*	k, $M^{-1}\ s^{-1}$
3.0	HCl*	1.2×10^{-5}	6.9×10^{-5}	10^{-5}	—	2.82×10^{5}
4.0	citrate	1.1×10^{-5}	1.1×10^{-4}	10^{-5}	—	1.09×10^{6}
4.3†	H_2SO_4†	1.1×10^{-5}	9.0×10^{-5}	—	10^{-5}	†
4.5†	H_2SO_4†	1.1×10^{-5}	6.1×10^{-5}	10^{-5}	—	†
5.0	citrate	1.1×10^{-5}	3.1×10^{-5}	10^{-5}	—	1.07×10^{7}
5.5†	H_2SO_4	8.0×10^{-6}	5.3×10^{-6}	10^{-5}	10^{-5}	†

*Concentration buffered.
†Unbuffered system; *p*H given at beginning of reaction. Meaningful rate constants cannot be determined (see text).

observed. Their experiments were conducted, as were those of *Larson et al.*, by bubbling gaseous ozone through S(IV) reactant solutions and analyzing periodically for unreacted S(IV) by West-Gaeke colorimetry. In their study, aqueous ozone concentrations would be, if equilibrium prevailed, about 3 orders of magnitude lower than those of the present study. But whether the observed differences in catalytic behavior between these studies is due to such concentration differences is uncertain. Several possibilities have already been mentioned that could account for the low rate constants obtained by Larson et al. In addition to these, in Harrison et al.'s experiments, the presence of the transition metal ions could be affecting the analysis for S(IV). For example, heavy metals are known to interfere with the West-Gaeke method, and addition of EDTA (ethylenediaminetetraacetic acid) is recommended by some to reduce such interferences [*Zurlo and Griffini*, 1962; *Scaringelli et al.*, 1967].

3.5. *Inhibition Studies*

A wide variety of organic compounds, and even some inorganics, are known to inhibit the autooxidation of S(IV) [*Huss et al.*, 1978; *Altwicker*, 1979, 1980]. Particularly effective among these are the dihydroxybenzenes, especially hydroquinone, a free-radical scavenger. This inhibition is consistent with the general view that S(IV) autooxidation proceeds by the free-radical chain mechanism of *Bäckström* [1934]. An attempt was made, therefore, to determine the effect of hydroquinone (HQ) on the rate of ozonation of S(IV).

Since hydroquinone itself is readily oxidized by ozone, it was necessary to establish its kinetics first. Experiments were conducted at 10°C with $I = 0.01$ *M* and *p*H of 3.0 and 5.0, with initial $[O_3]_0 \simeq 1.5 \times 10^{-5}$ *M*. Under pseudo first-order conditions, reaction order with respect to O_3 was determined to be unity (based on the linearity of plots of ln $[O_3]$ vs. time). For the range of HQ concentrations employed, the data conform well to the rate law $r_{HQ} = k_{HQ}[HQ][O_3]$ (see Table 4). This second-order rate law is in agreement with that customarily found for the ozonation of organics [*Hoigné and Bader*, 1978]. No data for k_{HQ} have been found in the literature, but the present value of about $1.5 \times 10^{7}\ M^{-1}\ s^{-1}$ (Table 4) is considerably larger than the values of about $4\ M^{-1}\ s^{-1}$ reported for benzene, $10^{3}\ M^{-1}\ s^{-1}$ for phenol, and $4 \times 10^{3}\ M^{-1}\ s^{-1}$ for *o*-cresol (all at an unspecified low *p*H, presumably at 25°C) [*Hoigné and Bader*, 1978]. Noteworthy in Table 4 is that k_{HQ} is virtually the same at both *p*H levels investigated. This indicates the absence of acid-base catalysis and is consistent with ozonation through direct attack by ozone rather than by intermediate radical species produced by hydroxide-ion catalyzed decomposition of ozone.

For studying S(IV) oxidation in the presence of HQ, mixtures of HQ and S(IV) were prepared with reactant in sufficient excess relative to O_3 to maintain pseudo first-order conditions. Overall ozone consumption is then given by

$$r = k_{HQ}[HQ][O_3] + k^*[S(IV)][O_3] = k_{1T}[O_3] \qquad (6)$$

where k^* is the second-order rate constant for the ozonation of S(IV) in the presence of HQ, and k_{1T} is the pseudo first-order rate constant for the overall reaction. Values of k^* calculated with (6) are listed in Table 5 along with estimates of probable error, presumed to propagate through the calculations as rms error. These calculated values of k^* are compared with the rate constants from Figure 3 as the ratio k^*/k, where a value of unity indicates no effect from HQ. Results obtained with the lowest HQ concentration are believed to be more reliable because smaller absorbence uncertainties for HQ absorption are involved and because smaller relative error is likely to occur in calculating k^* from (6). At this lowest concentration the results for both *p*H levels suggest k^* to be on the order of only 25% lower than k, while all the data combined suggest k^* to be on the order of one-half k. Unfortunately, because of the relatively large uncertainties and low reproducibilities associated with the data, a firm conclusion based on these data is not possible. However, of some significance is that the results obtained at the two different *p*H levels are much the same. If ozonation proceeded by a free-radical chain mechanism, the inhibiting effect of HQ would be expected to be greater at the higher *p*H, where the free-radical concentration (produced by the decomposition

TABLE 4. Rate Constants for Hydroquinone-Ozone Reaction

	$k_{HQ} \times 10^{-7}$ $M^{-1}\ s^{-1}$	
$[HQ]_0$, *M*	*p*H 3.0*	*p*H 5.0†
1.67×10^{-5}	1.19	1.20
1.67×10^{-5}	1.61	1.62
1.67×10^{-5}	1.39	1.56
3.33×10^{-5}	1.65	1.55
3.33×10^{-5}	1.21	1.80
3.33×10^{-5}	1.61	—
5.0×10^{-5}	1.33	1.47
5.0×10^{-5}	1.43	1.75
5.0×10^{-5}	1.53	1.64
	1.44 ± 0.2	1.57 ± 0.2

Data for 10°C, ionic strength 0.01 *M*, initial ozone concentration 1.5×10^{-5} *M*, and monitoring wavelength 272 nm.
*H_2SO_4 concentration buffered.
†Citrate buffer.

TABLE 5. Rate Constants for Sulfur (IV)-Ozone Reaction Determined in the Presence of Hydroquinone

pH	$[HQ]_0$, M	$[S(IV)]_0$, M	k_{1T}, s^{-1}	$k^* \times 10^{-5}$, $M^{-1}\,s^{-1}$†	k^*/k‡
3.0	1.67×10^{-5}	1.7×10^{-3}	580 ± 87	2.06 ± .55	0.72 ± 0.20
3.0	1.67×10^{-5}	9.9×10^{-4}	397 ± 60	1.65 ± .70	0.57 ± 0.24
3.0	1.67×10^{-5}	7.7×10^{-4}	424 ± 64	2.47 ± .94	0.86 ± 0.33
3.0	3.33×10^{-5}	1.3×10^{-3}	503 ± 75	0.28 ± .76	0.10 ± 0.28
3.0	3.33×10^{-5}	1.5×10^{-3}	839 ± 143	2.46 ± .95	0.91 ± 0.35
3.0	3.33×10^{-5}	1.1×10^{-3}	566 ± 85	0.90 ± .98	0.31 ± 0.34
3.0	3.33×10^{-5}	1.7×10^{-3}	678 ± 102	1.23 ± .71	0.43 ± 0.25
3.0	5.0×10^{-5}	2.3×10^{-3}	934 ± 205	1.04 ± 1.01	0.36 ± 0.35
5.0	1.67×10^{-5}	2.9×10^{-5}	465 ± 70	68.8 ± 26.9	0.79 ± 0.37
5.0	3.33×10^{-5}	5.7×10^{-5}	816 ± 131	49.3 ± 25.6	0.56 ± 0.32
5.0	5.0×10^{-5}	7.2×10^{-5}	1005 ± 251	28.7 ± 37.8	0.33 ± 0.44

Data for 10°C, ionic strength 0.01 M, initial ozone concentration 1.5×10^5 M, and monitoring wavelength 272 nm.

†Calculated from (6).

‡Using, from Figure 3, k(at pH 3) = (2.87 ± .14) × 10^5 $M^{-1}\,s^{-1}$, and k(at pH 5) = (8.73 ± 2.25) × 10^6 $M^{-1}\,s^{-1}$.

of ozone) is expected to be greater. This does not appear to be the case.

In their recent study, *Martin and Damschen* [1982] report the rate of the S(IV)-O_3 reaction to be insensitive to ethanol, acetone, formaldehyde, and acetic acid, each representative of a class of the many diverse organic compounds known to inhibit S(IV) autooxidation, presumably by functioning as radical chain terminators [*Altwicker*, 1979, 1980]. Furthermore, in agreement with the present results, they also observe no catalysis by metal ions. Hence, it is considered likely, on the basis of the present results and those of *Martin and Damschen* [1982], that the S(IV)-O_3 reaction proceeds by other than a free-radical chain mechanism. A similar conclusion was reached by *Martin and Damschen* [1981] for the oxidation of S(IV) by hydrogen peroxide.

4. MECHANISM

For the ozonation of S(IV) in solution, *Penkett et al.* [1979] propose the free radical mechanism

$$2O_3 + OH^- \rightarrow HO^{\cdot} + O_2^{-\cdot} + 2O_2 \qquad (7a)$$

$$HO^{\cdot} + HSO_3^- \rightarrow HSO_3^{\cdot} + OH^- \qquad (7b)$$

$$HSO_3^{\cdot} + O_2 \rightarrow HSO_5^{\cdot} \qquad (7c)$$

$$HSO_5^{\cdot} + HSO_3^- \rightarrow HSO_3^{\cdot} + HSO_5^- \qquad (7d)$$

$$HSO_5^- + HSO_3^- \rightarrow 2HSO_4^- \qquad (7e)$$

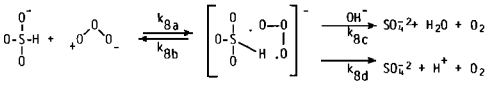
$$HSO_5^{\cdot} + HSO_5^{\cdot} \rightarrow \text{termination} \qquad (7f)$$

where the propagation and oxidation steps (7*c*)–(7*e*) are the same as those for *Bäckström*'s [1934] mechanism for autooxidation. The initiation step (7*a*), although energetically feasible, finds little support in the literature [see, for example, *Weiss*, 1935; *Alder and Hill*, 1950; *Kilpatrick et al.*, 1956; *Ivanov et al.*, 1972; *Peleg*, 1976; *Razumovskii et al.*, 1979] and appears to have been proposed largely because it provides a source of O_2, conveniently allowing subsequent application of Bäckström's mechanism. Another weakness of Penkett et al.'s mechanism is that in spite of their contention to the contrary the transfer of two oxygen atoms from each ozone molecule to each product sulfate molecule (required by the tracer studies of *Espenson and Taube* [1965]), is not accounted for. *Larson et al.* [1978] also presume a reaction involving somewhat the same sulfur radicals as in the Bäckström mechanism, but they do not elaborate.

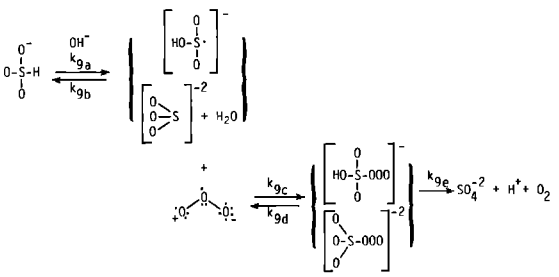
Erickson et al. [1977], while not proposing a mechanism, presume ozonation of the three possible S(IV) species in solution to proceed in parallel and at substantially different rates. Experimentally, they find (see (3)) $k_{SO_3^{-2}}/k_{HSO_3^-}$ to be on the order of 7000, concluding that above pH 3 most of the oxidation occurs through SO_3^{-2}, despite its very low concentration. If this interpretation is correct, oxidation of S(IV) by OH radical produced from the decomposition of O_3 in water [e.g., see *Peleg*, 1976, and others] can be ruled out, since OH radical oxidizes both HSO_3^- and SO_3^{-2} at substantially the same rate: $k_{HSO_3^- - OH} = 9.5 \times 10^9$ $M^{-1}\,s^{-1}$, $k_{SO_3^{-2} - OH} = 5.5 \times 10^9$ $M^{-1}\,s^{-1}$ [*Farhataziz and Ross*, 1977].

Results from the present study can be used to speculate on a possible mechanism for S(IV) oxidation. In this it is understood that since O_3, rather than S(IV), was monitored in the experiments, the implication is that the rate of S(IV) oxidation is equal to the rate of O_3 disappearance. This assumption is similarly implicit in the studies by *Erickson et al.* [1977], *Penkett et al.* [1979], and *Martin and Damschen* [1982], and seems sufficiently reasonable. Ozone loss by self-decomposition is extremely slow relative to its rate of disappearance following S(IV) addition, and since S(IV) itself is readily oxidized, it is reasonable that the rapid rate of O_3 disappearance in the presence of S(IV) is occasioned by the S(IV) reacting with the O_3 and that the rate of this reaction is equal to the rate of O_3 disappearance. Nonetheless, the possibility is recognized that S(IV) oxidation could, by some sequence of intermediate steps, proceed at a rate somewhat different from that observed for O_3.

Results obtained in the present study, and those of *Martin and Damschen* [1982], suggest a non-free-radical process: (1) no photoexcitation by strong, broad-spectrum UV radiation; (2) no catalysis by transition metals, often effective initiators of free-radical reactions; and (3) lack of substantial inhibition by a variety of antioxidants, typically free-radical scavengers. Further, the observed effect of ionic strength on the reaction rate constant (Figure 4 and the Appendix) is consistent with a reaction between two univalent negative species. For the predominant S(IV) species in solution (i.e., bisulfite ion), a reaction scheme compatible with these observations is



(8)



(9)

In reaction sequence (8), the S-H bond is assumed to be broken by direct ozone insertion analagous to insertion reactions for Si-H and C-H bonds [*Austin and Spialter*, 1968; *Bailey*, 1972; *Spialter et al.*, 1972]. This is followed by either spontaneous or hydroxide-ion catalyzed decomposition of the ozone adduct to give sulfate. In sequence (9), bisulfite ion undergoes either hydroxide-ion catalyzed rearrangement to its less abundant tautomer $HOSO_2^-$ (*Guthrie* [1979] estimates $[H\text{-}SO_3^-]/[HOSO_2^-] = 40$) or hydroxide-ion initiated proton removal to SO_3^{-2}. Both $HOSO_2^-$ and SO_3^{-2} possess an unshared pair of electrons on the S atom, making this a site capable of electrophilic attack by the terminal oxygen atom of the ozone molecule. As before, the ozone adducts so formed subsequently decompose to sulfate. Assuming reaction sequences (8) and (9) to occur simultaneously, the overall rate expression is

$$r = \left(\frac{k_{8a}k_{8d} + k_{8a}k_{8c}[OH^-]}{k_{8b} + k_{8d} + k_{8c}[OH^-]} + \frac{k_{9a}k_{9c}k_{9e}[OH^-]}{k_{9b}(k_{9d} + k_{9e}) + k_{9c}k_{9e}[O_3]}\right)[HSO_3^-][O_3]$$

For $k_{9c}k_{9e}[O_3] \ll k_{9b}(k_{9d} + k_{9e})$, reasonable for the low concentrations of O_3 employed, and for $k_{8b} \gg k_{8c}[OH^-]$, this expression reduces to the form

$$r = (k_{10a} + k_{10b}[OH^-])[HSO_3^-][O_3] \quad (10)$$

Whereas (1) and (2) are purely empirical representations of the present data over the *p*H range 3.0 to 6.2, (10) should be more general. Fitting the low *p*H rate constant data of *Erickson et al.* [1977], *Penkett et al.* [1979], and *Martin and Damschen* [1982] along with the data from the present study by this equation, $k_{10a} = 3.8 \times 10^5\ M^{-1}\ s^{-1}$ and $k_{10b} = 1.05 \times 10^{16}\ M^{-2}\ s^{-1}$ is obtained over the *p*H range 1 to 6.2 at 25°C. A plot of (10) on Figure 5, using these rate constants, produces a curve precisely overlying the curves shown for Erickson et al. and Penkett et al. at the lower *p*H and the curve shown for the present study at higher *p*H.

That the low-*p*H data are successfully represented by (10) implies either that ozone reacts with $SO_2 \cdot aq$ only slowly in comparison with bisulfite or that its contribution to the overall reaction is catalyzed by hydroxide ion, since for either situation the corresponding rate expression is equivalent in form to (10). It is noted that if $SO_2 \cdot aq$ ozonation does contribute measurably at low *p*H, reaction schemes (8) and (9) predict the overall second-order rate constant to vary only weakly with ionic strength, since $SO_2 \cdot aq$ and its ozone adduct are electrically neutral.

Comparison of the present rate expression with the last two terms of Erickson et al.'s rate expression (3) reveals the two expressions to be mathematically equivalent following introduction of the second dissociation constant for S(IV). Unlike Erickson et al.'s expression, however, the present expression is based on a proposed mechanism. It accounts for the observed effect of ionic strength on reaction rate and is based on the reaction proceeding through the predominant S(IV) species in solution, namely HSO_3^-. In contrast, Erickson et al.'s rate expression is strictly empirical, and further, implies that the reaction proceeds largely through the trace species SO_3^{-2}, raising the interesting question as to why. For purposes of rate calculations, however, the two expressions represent the data almost equally well, except above *p*H 4, where (10) is preferred because of its foundation on experimental data in this region.

Figure 6 shows a plot of available data for activation energy as a function of *p*H, which values can be used in conjunction with (10). As mentioned previously, Penkett et al.'s result at *p*H 5 is considered questionable. Below *p*H 3, the spread is noted to be fairly large. But inspection of the rate constant data of Erickson et al. in their Table 2 indicates their reported values to be too large. Recalculation from their Table 2 gives, at *p*H 0.6, 2.5 kcal/mol; at *p*H 2.1, 2.6 kcal/mol; at *p*H 3.1, 19.6 kcal/mol; and at *p*H 3.7, a negative activation energy. Using zero for the activation energy at *p*H 3.7, an average of these values is 6.2 kcal/mol, a more reasonable value in comparison with the other data in Figure 4.

As a final comment, reaction schemes (8) and (9) do not elucidate how an average of one and a half to two oxygen atoms from each ozone molecule is transferred to each product sulfate molecule, as required by the tracer studies of Espenson and Taube. However, this transfer can be envisioned to occur by rearrangement of the ozone adducts preceding or accompanying decomposition. Such rearrangement, in any event, seems easier to envision than excess oxygen transfer accompanying oxidation by free-radical intermediates. In forming the ozone adducts it may be tempting to presume attack on the S atom by the central oxygen atom of the ozone molecule, but this is to be resisted because in all canonical forms of ozone the central atom is surrounded by a full complement of eight electrons and, hence, cannot be electrophilic [*Bailey et al.*, 1959]. Furthermore, experimental evidence for such attack is lacking [e.g., see *Bailey et al.*, 1959; *Gould*, 1968, 1972; *Evans*, 1977; *Bailey*, 1978]. Other than in these elusive details of excess oxygen transfer, the reaction scheme outlined in (8) and (9) is compatible with known experimental observations.

5. Application to the Nonurban Troposphere

In Figure 5 the present results for the oxidation of S(IV) in solution by ozone are compared at 25°C with literature data for oxidation by hydrogen peroxide at representative gas-phase concentrations of ozone and hydrogen peroxide in the nonurban troposphere. Although these ozone concentrations vary with latitude, measurement site, altitude, season, time of day, and occasionally stratospheric intrusion, most values in the nonurban troposphere lie in the range 20–60 ppb [*Kelly and Stedman*, 1979; *Hansen and Padgett*, 1980; *Worth and Rippert-on*, 1980; *Routhier et al.*, 1980; *Shumate et al.*, 1981; *Martin and Barber*, 1981; *Johnson and Viezee*, 1981; *Seiler and Fishman*, 1981]. For purposes of comparison we adopt the often used value of 50 ppb [*Erickson et al.*, 1977; *Larson et al.*, 1978; *Penkett et al.*, 1979; *Möller*, 1980]. This value, in conjunction with a Henry's Law constant for ozone of about 0.01 *M*/atm at 25°C [*Kilpatrick et al.*, 1956; *Matrozov et al.*, 1975], gives an equilibrium cloud water concentration of $5 \times 10^{-10}\ M$.

For hydrogen peroxide a representative liquid-phase concentration is considerably less certain. This is due, in part, to a

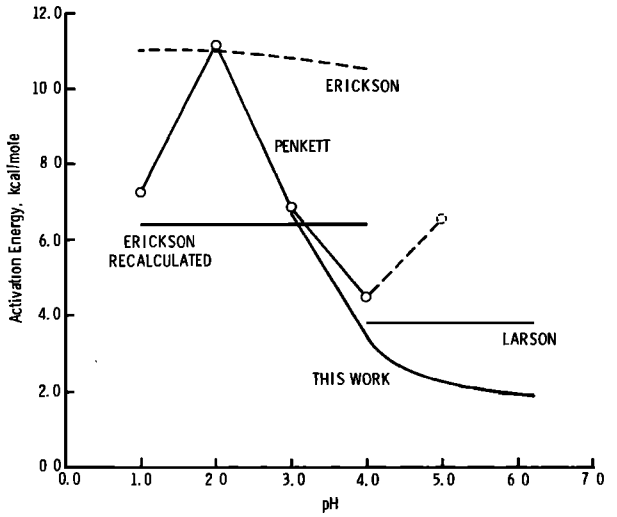


Fig. 6. Activation energy as a function of solution *p*H. The values from *Erickson et al.* [1977] and *Larson et al.* [1978] are derived from reported rate expressions; the values for *Penkett et al.* [1979] are reported data. Activation energies for Erickson et al. have been recalculated as described in the text. The dashed lines denote questionable values.

paucity of reliable data but also to uncertainty as how best to treat H_2O_2 equilibrium within a cloud. If reported gas-phase concentrations of H_2O_2 in rural air of from 0.3 to 3 ppb [*Kelly and Stedman*, 1979] were totally absorbed within the droplet phase of a cloud having liquid water content 1 ml/m^3 [*Kok*, 1980], the resulting H_2O_2 aqueous concentrations would be 1.3×10^{-5} *M* to 1.3×10^{-4} *M*. Yet actual measurements in rainwater (admittedly not cloud water) are considerably less [*Kok*, 1980; *Bufalini et al.*, 1979]. Furthermore, seasonal variations (in rainwater) can be substantial: from a high of 5.9×10^{-6} *M* in summer to a low of 5.9×10^{-8} *M* in winter, as measured in the Research Triangle area of North Carolina [*Bufalini et al.*, 1979]. Because of the extremely large Henry's Law constant for H_2O_2 (on the order of 7.1×10^4 *M*/atm 25°C [*Martin and Damschen*, 1981]), it is not entirely clear how best to estimate the concentration of H_2O_2 in cloud droplets on the basis of gas-phase measurements outside a cloud. For example, a droplet phase concentration of 4.3×10^{-5} *M* corresponds to a gas-phase concentration of 1 ppb if, on the one hand, all gas-phase H_2O_2 is assumed to be dissolved in a cloud with 1 ml/m^3 water content [*Penkett et al.*, 1979], or, on the other hand, to a gas-phase concentration of 0.61 ppb if equilibrium is assumed [*Martin and Damschen*, 1981]. In view of these uncertainties, for the present purposes of estimating relative S(IV) oxidation rates by O_3 and H_2O_2, we assume a representative upper-limit liquid-phase H_2O_2 concentration of 4.3×10^{-5} *M* and a lower-limit value of 4.3×10^{-6} *M*. This latter value corresponds more closely with the highest concentrations measured by Bufalini et al in rainwater.

Specific reaction rates for S(IV) oxidation by H_2O_2 at these two concentration levels are plotted in Figure 5, using the rate expression of *Martin and Damschen* [1981], at 25°C

$$r = 5.2 \times 10^6 [H^+][HSO_3^-][H_2O_2]/(0.1 + [H^+]) \quad (11)$$

valid over the *p*H range 0–7.5. From this figure the relative importance of O_3 and H_2O_2 oxidation as a function of *p*H can be assessed. For the higher H_2O_2 concentration the present experimental results indicate significant competition by O_3 at about *p*H 5; for the lower H_2O_2 concentration, competition becomes important at about *p*H 4.5. At *p*H 5.5, oxidation by O_3 dominates, and at *p*H 6 it dominates by possibly 2 or more orders of magnitude.

The relevance of this comparison of S(IV) oxidation rates by O_3 and H_2O_2 to the conversion of SO_2 within nonurban tropospheric clouds depends to a large extent on the cloud water *p*H levels typically occurring within these clouds. Accurate *p*H measurements on cloud water are limited, particularly measurements based on airborne sampling free of ground influences. However, such data that are available indicate cloud water *p*H levels roughly in the range 3.5–7.3 [*Falconer and Falconer*, 1981; *Hegg and Hobbs*, 1981]. Reasonable mean *p*H values for such cloud water measurements seem to be on the order of 5.1 ± 0.9 [*Hegg and Hobbs*, 1981]. Close examination of such data suggests that cloud water *p*H in the range 5–6 tend to be associated with the nonurban environment, whereas *p*H levels below 5 tend to be more associated with polluted air [*Hegg and Hobbs*, 1979]. (It may be of interest to note that whereas cloud water *p*H measurements based on ground sampling span roughly the same *p*H range as those based on airborne sampling, a higher frequency of lower *p*H tends to be associated with ground-based data, and the mean *p*H for these data is somewhat lower—on the order of 4.5. However, ground influences likely have an effect here, and such data are not likely to be truly representative of the free troposphere [*Hegg and Hobbs*, 1981].) Consideration of the above cloud water *p*H levels in relation to the oxidation rates by O_3 and H_2O_2 plotted in Figure 5 indicates the potential importance of O_3 as a contributor to the overall oxidative conversion of SO_2 within typical nonpolluted tropospheric clouds.

Cloud water temperatures are generally well below the 25°C at which the comparison in Figure 5 is made. However, the rate expression of *Martin and Damschen* [1981] for H_2O_2 is valid only at 25°C. Moreover, the effect of temperature on the overall conversion rate of S(IV) by H_2O_2 in cloud droplets is difficult to assess unambiguously [*Martin and Damschen*, 1981]. However, using activation energies from Penkett et al. (on the order of 8 kcal/mol at *p*H 5.5), and assuming an invariant liquid-phase H_2O_2 concentration with temperature, a reduction in rate of about 50% is indicated for a decrease in temperature from 25°C to 10°C. But, because of the large increase in Henry's Law constant for H_2O_2 with decreasing temperature [*Martin and Damschen*, 1981], there may be an actual net increase in specific oxidation rate. Neither the direction nor the magnitude of the net temperature effect can be properly assessed until data on actual concentrations of H_2O_2 in cloud water become available. For ozone, the present data indicate a decrease in reaction rate of roughly 20% from 25°C to 10°C; but coupled with the fact that at 10°C the Henry's Law solubility constant for ozone is on the order of 80% higher [*Matrozov et al.*, 1975], given the same gas-phase ozone concentration, the net specific oxidation rate is larger at 10°C than at 25°C by about 45%.

The oxidation of S(IV) in cloud droplets by dissolved molecular oxygen is expected to be much slower than that by ozone. For example, by applying what appears to be by far the largest rate constant reported in the literature for the autoxidation of S(IV), namely that of *McKay* [1971], a specific oxidation rate over the *p*H range 4–7 is obtained that closely follows the straight-line extrapolation for ozone shown for Penkett et al. in Figure 5. In some cases, however, catalysis by transition metals can lead to an even faster rate. At *p*H 6 and for 10^{-4} *M* Mn(II) plus 10^{-4} *M* Fe(II) in solution, the extremely large catalytic effects reported by *Barrie and Georgii* [1976] predict a catalyzed O_2 rate almost 10^4 times that shown in Figure 5 for

ozone. Although these catalyst concentrations are much larger than expected in the rural atmosphere [*Hegg and Hobbs*, 1978], it is clear that catalyzed O_2 oxidation could, under some circumstances, compete with oxidation by ozone.

For very rapid aqueous-phase reactions, transport limitations to and within cloud droplets possibly can become an important consideration [*Martin and Damschen*, 1981; *Schwartz and Freiberg*, 1981; *Schwartz*, 1983]. As an example, at *p*H 6, for the present O_3 rate constants and a gas-phase SO_2 concentration of 50 ppt, application of Schwartz's criteria indicates oxidation within a 10-μm radius cloud droplet to be partially transport limited by ozone diffusion in the droplet. Since this transport limitation decreases rapidly as droplet size decreases (as the square of the radius), droplet size distribution can play a significant role in determining the overall conversion rate within a cloud. Another consideration of possible importance in cloud droplets is the potentially limiting effect on interphase transport imposed by the organic films that sometimes cover the surface of aqueous aerosols [*Graedel and Weschler*, 1981].

6. Recommendations

Application of the present kinetic results for predicting SO_2 conversion rates within cloud droplets carries with it the implied assumption that the rate expression and rate constants obtained experimentally at about 10^{-6} M ozone (the lowest concentration at which the rate constants could be effectively measured) are valid at cloud water concentrations on the order of 5×10^{-10} M, a factor of 2000 smaller. Because of this required large extrapolation in concentration, even a relatively small uncertainty in ozone reaction order can have a large effect. For example, if instead of unity, the reaction order with respect to ozone were really 0.7, the corresponding ozonation rate at cloud water concentrations would be 10 times that shown in Figure 5. On the other hand, if the reaction order were really 1.3, the corresponding rate would be one tenth that indicated. Although first-order kinetics were also found by *Larson et al.* [1978] in their kinetic studies at low ozone concentrations, their rate constants are much lower, giving rise to possible suspicions of a concentration effect. Hence, these very different results are in need of resolution by an alternative independent experimental technique employing ozone concentrations closer to those actually expected in cloud water. A similar need does not exist for S(IV) (or for H_2O_2, for that matter) because experimental concentrations have been more acceptably representative of those expected in cloud water.

It is noted that at the representative mean *p*H of 5 for cloud water, ozone is a far more powerful oxidizer than H_2O_2; for example, $k_{O_3} = 1.04 \times 10^7\ M^{-1}\ s^{-1}$ as compared with $k_{H_2O_2} = 5.20 \times 10^2\ M^{-1}\ s^{-1}$ (equations (10) and (11) at 25°C). Hence, oxidation of S(IV) by H_2O_2 in cloud water competes with that by ozone only because H_2O_2 is present in high concentration relative to ozone. This fact points to the clear need for accurate data on H_2O_2 concentrations in cloud water, not presently available. For ozone, the more important need is that its kinetics be known accurately.

7. Conclusions

Rate constants measured in the present investigation show the rate of ozonation of S(IV) in aqueous solution at *p*H above 4 to be much faster than previous experimental data indicate. Application of these rate constants to SO_2 conversion in cloud water predicts conversion rates by ozone to be competitive with those by H_2O_2 at *p*H above about 4.5 and to dominate at *p*H above about 5.5. Since these *p*H's are typical for nonurban tropospheric cloud water, ozone is a potentially important contributor to the overall oxidative conversion of SO_2 to sulfate in the nonurban troposphere. The rate of ozone conversion within cloud droplets is not expected to be influenced by the presence of transition metals, soluble trace organics (except as a film inhibiting transport), or solar intensity. An increase in solution ionic strength increases oxidation rate, but not markedly. Reaction proceeds other than by a free-radical mechanism, likely by direct electrophilic ozone attack on the S atom of the bisulfite ion, the sulfite ion, or both. The reaction is catalyzed by hydroxide ion.

Appendix. Dependence of Reaction Rate on Ionic Strength

In reactions involving ionic species, changes in solution ionic strength alter the activity coefficients of the reactants and the reaction intermediates, thereby influencing reaction rate. Both the primary and secondary kinetic salt effects can be expressed by an equation of the form [e.g., see *Glasstone*, 1946] $\log k = \log k_0 + \log Q(\gamma_i)$, where k is the reaction rate constant, k_0 is the reaction rate constant at infinite dilution, and $Q(\gamma_i)$ is a quotient of activity coefficients γ_i appropriate to the particular chemical process. Since many mean activity coefficients correlate reasonably well by the proportionality [*Davies*, 1962] $\log \gamma_\pm \propto (I^{1/2}/(1 + I^{1/2}) - 0.3\ I)$ (at least at lower ionic strengths), k can reasonably be expected to vary with I as $\log k = \log k_0 + m(I^{1/2}/(1 + I^{1/2}) - 0.3\ I)$, where m is a constant, either positive or negative.

For the primary salt effect, $m = z_A z_B$, where z_i is the ionic charge of reactant i with its appropriate algebraic sign. Accordingly, an elementary reaction between two univalent negative ions has $m = +1$. For the secondary salt effect, where a nonionic reaction is catalyzed by an ionic species, say, hydroxide ion, $k \propto [OH^-]$. Using the activity product constant of water $K_w = a_{H^+}a_{OH^-} = a_{H^+}[OH^-]\gamma_{OH^-}$, it can be shown that for constant *p*H (i.e., constant H^+ activity) $\log k = \log k_0 - \log \gamma_{OH^-}$. Using Davies' correlation for estimating the individual activity coefficient γ_{OH^-}, gives $\log k = \log k_0 + 0.5(I^{1/2}/(1 + I^{1/2}) - 0.3\ I)$, or $m = +0.5$. For a noncatalyzed reaction involving at least one neutral species, say O_3, it can be shown that $\log k = \log k_0 + \beta I$, where β is the salting coefficient for O_3. For the present data, plots of $\log k$ vs. I are distinctly nonlinear and, further, require β to be on the order of 1.5–2 M^{-1}, whereas β determined experimentally by absorbing gaseous ozone in solutions of different ionic strength (at *p*H 5 and 25°C) is on the order of 0.1 M^{-1}, comparable with β for many common gases (0.01 to 0.1 M^{-1} [*Harned and Owen*, 1958]). In view of the foregoing considerations the near unity slopes in Figure 4 suggest (although do not prove) that ozonation of S(IV) in solution involves reaction between two univalent negative species.

Acknowledgments. The author wishes to thank T. A. Grepiotis for his dedicated assistance in the laboratory and W. R. Cofer III for his helpful discussions and his critical reading of the manuscript.

References

Alder, M. G., and G. R. Hill, The kinetics and mechanism of hydroxide ion catalyzed ozone decomposition in aqueous solution, *J. Am. Chem. Soc.*, *72*, 1884–1886, 1950.

Altwicker, E. R., Oxidation/inhibition of sulfite ion in aqueous solution, *AIChE Symp. Ser.*, *75* (188), 145–150, 1979.

Altwicker, E. R., Oxidation and oxidation-inhibition of sulfur dioxide, in *Advances in Environmental Science and Engineering*, vol. 3, pp. 80–91, Gordon and Breach Science Publishers, New York, 1980.

Austin, J. D., and L. Spialter, Substituent effects in the oxidative cleavage of organosilanes by ozone, in *Advances in Chemistry Series 77, Oxidation of Organic Compounds*, vol. 3, *Ozone Chemistry, Photo and Singlet Oxygen and Biochemical Oxidations*, edited by R. F. Gould, pp. 26–31, American Chemical Society, Washington, D. C., 1968.

Bäckström, H. L. J., The chain mechanism in the autoxidation of sodium sulfite solutions, *Z. Phys. Chem. (Leipzig), B25*, 122–138, 1934.

Bailey, P. S., Preface, in *Advances in Chemistry Series 112, Ozone Reaction with Organic Compounds*, edited by R. F. Gould, p. ix, American Chemical Society, Washington, D. C., 1972.

Bailey, P. S., Organic groupings reactive toward ozone: Mechanisms in aqueous media, in *Ozone in Water and Wastewater Treatment*, edited by F. L. Evans III, pp. 29–59, Ann Arbor Science, Ann Arbor, Mich., 1977.

Bailey, P. S., *Ozonation in Organic Chemistry*, vol. 1, *Olefinic Compounds*, Academic, New York, 1978.

Bailey, P. S., S. S. Bath, and J. B. Ashton, Initial attack of ozone on an unsaturated system, *Advances in Chemistry Series 21, Ozone Chemistry and Technology*, pp. 143–148, American Chemical Society, Washington, D. C., 1959.

Barrie, L. A., and H. W. Georgii, An experimental investigation of the absorption of sulfur dioxide by water drops containing heavy metal ions, *Atmos. Environ., 10*, 743–749, 1976.

Beilke, S., and G. Gravenhorst, Heterogeneous SO_2 oxidation in the droplet phase, *Atmos. Environ., 12*, 231–239, 1978.

Bufalini, J. J., H. T. Lancaster, G. R. Namie, and B. W. Gay, Jr., Hydrogen peroxide formation from the photooxidation of formaldehyde and its presence in rainwater, *J. Environ. Sci. Health, A14*, 135–141, 1979.

Davies, C. W., *Ion Association*, pp. 39–41, Butterworth, Washington, D. C., 1962.

Erickson, R. E., L. M. Yates, R. L. Clark, and D. McEwen, The reaction of sulfur dioxide with ozone in water and its possible atmospheric significance, *Atmos. Environ., 11*, 813–817, 1977.

Espenson, J. H., and H. Taube, Tracer experiments with ozone as oxidizing agent in aqueous solution, *Inorg. Chem., 4*, 704–709, 1965.

Evans, F. L., III (Ed.), *Ozone in Water and Wastewater Treatment*, Ann Arbor Science, Ann Arbor, Mich., 1977.

Falconer, R. E., and P. D. Falconer, Determination of cloud water acidity at a mountain observatory in the Adirondack Mountains of New York State, *J. Geophys. Res., 85*, 7465–7470, 1980.

Farhataziz, and A. B. Ross, Selected specific rates of reactions of transients from water in aqueous solution, 3, Hydroxyl radical and perhydroxyl radical and their radical ions, *Rep. NSRDS-NBS 59*, Nat. Bur. Stand., Washington, D. C., 1977.

Glasstone, S., *Textbook of Physical Chemistry*, 2nd ed., pp. 956–960, 966–968, 1111–1118, 1134–1140, D. Van Nostrand, Princeton, N. J., 1946.

Gould, R. F. (Ed.), *Advances in Chemistry Series 77, Oxidation of Organic Compounds*, vol. 3, *Ozone Chemistry, Photo and Singlet Oxygen and Biochemical Oxidations*, American Chemical Society, Washington, D. C., 1968.

Gould, R. F. (Ed.), *Advances in Chemistry Series 112, Ozone Reactions with Organic Compounds*, American Chemical Society, Washington, D.C., 1972.

Graedel, T. E., and C. J. Weschler, Chemistry within aqueous atmospheric aerosols and raindrops, *Rev. Geophys. Space Phys., 19*, 505–539, 1981.

Guthrie, J. P., Tautomeric equilibria and pK_a values for 'sulfurous acid' in aqueous solution: A thermodynamic analysis, *Can. J. Chem., 57*, 454–457, 1979.

Hansen, A. G., and S. J. Padgett, An analysis of the vertical distribution of ozone in the atmosphere, final report, Scientex Corp., Washington, D. C., 1980.

Harrison, H., T. V. Larson, and C. S. Monkman, Aqueous phase oxidation of sulfites by ozone in the presence of iron and manganese, *Atmos. Environ., 16*, 1039–1041, 1982.

Harned, H. S., and Owen, B. B., *The Physical Chemistry of Electrolytic Solutions*, 3rd ed., pp. 531–532, 736, Reinhold, New York, 1958.

Hegg, D. A. and P. V. Hobbs, Oxidation of sulfur dioxide in aqueous systems with particular reference to the atmosphere, *Atmos. Environ., 12*, 241–253, 1978.

Hegg, D. A., and P. V. Hobbs, The homogeneous oxidation of sulfur dioxide in cloud droplets, *Atmos. Environ., 13*, 981–987, 1979.

Hegg, D. A., and P. V. Hobbs, Cloud water chemistry and the production of sulfates in clouds, *Atmos. Environ., 15*, 1597–1604, 1981.

Hoather, R. C., and C. F. Goodeve, The oxidation of sulphurous acid, 4, Catalysis by a glass powder containing manganese and iron, *Trans. Faraday Soc., 30*, 1156–1161, 1934.

Hoigné, J., and H. Bader, The role of hydroxyl radical reactions in ozonation processes in aqueous solutions, *Water Res., 10*, 377–386, 1976.

Hoigné, J., and H. Bader, Ozone initiated oxidations of solutes in wastewater: A reaction kinetic approach, *Progr. Water Tech., 10*, 657–671, 1978.

Huss, A., Jr., P. K. Lim, and C. A. Eckert, On the 'uncatalyzed' oxidation of sulfur (IV) in aqueous solutions, *J. Am. Chem. Soc., 100*, 6252–6253, 1978.

Ivanov, Y. E., G. P. Nikitina, M. F. Pushlenkov, and V. G. Shumkov, Ozone in aqueous solutions, 1, Kinetics and mechanism of the decomposition of ozone in water and in nitric acid solutions, *Russ. J. Phys. Chem., 46*, 1240, 1972.

Johnson, W. B., and W. Viezee, Stratospheric ozone in the lower troposphere, 1, Presentation and interpretation of aircraft measurements, *Atmos. Environ., 15*, 1309–1323, 1981.

Kelly, T. J., and D. H. Stedman, Measurements of H_2O_2 and HNO_3 in rural air, *Geophys. Res. Lett., 6*, 375–378, 1979.

Kilpatrick, M. L., C. C. Herrick, and M. Kilpatrick, The decomposition of ozone in aqueous solution, *J. Am. Chem. Soc., 78*, 1784–1789, 1956.

Kok, G. L., Measurements of hydrogen peroxide in rainwater, *Atmos. Environ., 14*, 653–656, 1980.

Larson, T. V., Secondary aerosol: Production mechanisms of sulfate compounds in the atmosphere, *Ann. N. Y. Acad. Sci., 338*, 26–38, 1980.

Larson, T. V., N. R. Horike, and H. Harrison, Oxidation of sulfur dioxide by oxygen and ozone in aqueous solution: A kinetic study with significance to atmospheric rate processes, *Atmos. Environ., 12*, 1597–1611, 1978.

Logan, J. A., M. J. Prather, S. C. Wofsy, and M. B. McElroy, Tropospheric chemistry: A global perspective, *J. Geophys. Res., 86*, 7210–7254, 1981.

Martin, A., and F. R. Barber, Sulphur dioxide, oxides of nitrogen and ozone measured continuously for 2 years at a rural site, *Atmos. Environ., 15*, 567–578, 1981.

Martin, L. R., and D. E. Damschen, Aqueous oxidation of sulfur dioxide by hydrogen peroxide at low *p*H, *Atmos. Environ., 15*, 1615–1621, 1981.

Martin, L. R., and D. E. Damschen, Kinetic studies of sulfite oxidation in aqueous solution, paper presented at 185th National Meeting, Am. Chem. Soc., Las Vegas, Nevada, March 28–April 2, 1982.

Matrozov, V. I., S. A. Kashtanov, A. M. Stepanov, and B. A. Tregubov, Solubility of ozone in water, *Zh. Prikl. Khimii, 48*, 1838–1841, 1975.

McKay, H. A. C., The atmospheric oxidation of sulphur dioxide in water droplets in presence of ammonia, *Atmos. Environ., 5*, 7–14, 1971.

Middleton, P., C. S. Kiang, and V. A. Mohnen, Theoretical estimates of the relative importance of various urban sulfate aerosol production mechanisms, *Atmos. Environ., 14*, 463–472, 1980.

Möller, D., Kinetic model of atmospheric SO_2 oxidation based on published data, *Atmos. Environ., 14*, 1067–1076, 1980.

Parry, E. P., and D. H. Hern, Stoichiometry of ozone-iodide reaction: Significance of iodate formation, *Environ. Sci. Technol., 7*, 65–66, 1973.

Peleg, M., The chemistry of ozone in the treatment of water, *Water Res., 10*, 361–365, 1976.

Penkett, S. A., B. M. R. Jones, K. A. Brice, and A. E. J. Eggleton, The importance of atmospheric ozone and hydrogen peroxide in oxidising sulphur dioxide in cloud and rainwater, *Atmos. Environ., 13*, 123–137, 1979.

Perrich, J., J. McCammon, L. Cronholm, M. Fleishman, J. Pavoni, and V. Riesser, Ozone disinfection and oxidation in a model ozone contacting reactor, *AIChE Symp. Ser., 73*(166), 225–229, 1977.

Razumovskii, S. D., V. S. Ovechkin, M. L. Konstantinova, and G. E. Zaikov, The kinetics of the reaction of ozone with hydroxyl ions in aqueous solution, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 289–293, 1979.

Routhier, F., R. Dennett, D. D. Davis, A. Wartburg, P. Haagenson, and A. C. Delany, Free tropospheric and boundary-layer airborne measurements of ozone over the latitude range of 58°S to 70°N, *J. Geophys. Res., 85*, 7307–7321, 1980.

Scaringelli, F. P., B. E. Saltzman, and S. A. Frey, Spectrophotometric determination of atmospheric sulfur dioxide, *Anal. Chem., 39*, 1709–1719, 1967.

Schwartz, S. E., Gas-aqueous reactions of sulfur and nitrogen oxides in

liquid-water clouds, in *SO_2, NO, and NO_2 Oxidation Mechanisms: Atmospheric Considerations*, edited by J. G. Calvert, Ann Arbor Science, in press, 1983.

Schwartz, S. E., and J. E. Freiberg, Mass-transport limitation to the rate of reaction of gases in liquid droplets: Application to oxidation of SO_2 in aqueous solutions, *Atmos. Environ.*, *15*, 1129–1144, 1981.

Seiler, W., and J. Fishman, The distribution of carbon monoxide and ozone in the free troposphere, *J. Geophys. Res.*, *86*, 7255–7265, 1981.

Shumate, M. S., R. T. Menzies, W. B. Grant, and D. S. McDougal, Laser absorption spectrometer: Remote measurement of tropospheric ozone, *Appl. Opt.*, *20*, 545–552, 1981.

Spialter, L., L. Pazdernik, S. Bernstein, W. A. Swansiger, G. R. Buell, and M. E. Freeburger, The ozone-hydrosilane reaction: A mechanistic study, in *Advances in Chemistry Series 112, Ozone Reactions with Organic Compounds*, edited by R. F. Gould, pp. 65–77, American Chemical Society, Washington, D. C., 1972.

Weiss, J., Investigations on the radical HO_2 in solution, *Trans. Faraday Soc.*, *31*, 668–681, 1935.

West, P. H., and G. C. Gaeke, Fixation of sulfur dioxide as disulfitomercurate (II) and subsequent colorimetric estimation, *Anal. Chem.*, *28*, 1816–1819, 1956.

Worth, J. J. B., and L. A. Ripperton, Rural ozone-sources and transport, in *Advances in Environmental Science and Engineering*, vol. 3, pp. 150–170, Gordon and Breach Science Publishers, New York, 1980.

Zurlo, N., and A. M. Griffini, Measurement of the sulfur dioxide content of the air in the presence of oxides of nitrogen and heavy metals, *Med. Lavoro*, *53*, 330–335, 1962.

(Received September 3, 1982;
revised March 3, 1983;
accepted March 7, 1983.)