

OXIDATION OF SULFUR DIOXIDE BY OXYGEN AND OZONE IN AQUEOUS SOLUTION: A KINETIC STUDY WITH SIGNIFICANCE TO ATMOSPHERIC RATE PROCESSES*

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Abstract—The oxidation rates of SO_2 by O_2 and O_3 have been studied in buffered aqueous solutions at pH between 4 and 12, temperatures between 5 and 25°C, oxygen partial pressures between 0.11 and 1.0 atm., and ozone partial pressures between 0.2 and 1.0 ppm. For the O_2 reaction we observe oxidation rates of the form:

$$\frac{d[\text{SO}_4^{2-}]}{dt} = \{k_1 + k_2[\text{H}^+]^{1/2} + k_3 P_{\text{O}_3}[\text{H}^+]^{-1}\} [\text{SO}_3^{2-}]$$

with

$$k_1 = (4.8 \pm 0.6) \times 10^{-3} \text{ s}^{-1}$$

$$k_2 = (8.9 \pm 1.0) \text{ s}^{-1} \text{ M}^{-1/2}$$

$$k_3 = (3.9 \pm 0.6) \times 10^{-12} \text{ s}^{-1} \text{ M atm}^{-1}, \text{ all at } 298 \text{ K}$$

with a multiple correlation coefficient (R^2) = 0.73.

In acidic solutions this expression displays weak temperature dependence and zero-order O_2 dependence. For the O_3 reaction we observe oxidation rates of the form:

$$\frac{d[\text{SO}_4^{2-}]}{dt} = k_4 K_{\text{HO}_3} P_{\text{O}_3} [\text{HSO}_3^-] [\text{H}^+]^{-0.1 \pm 0.02}$$

with

$$k_4 = (4.4 \pm 2.0) \times 10^4 \text{ M}^{-0.9} \text{ s}^{-1}$$

$$K_{\text{HO}_3} = 0.0123 \text{ M atm}^{-1}, \text{ both at } 298 \text{ K},$$

with $R^2 = 0.38$. A simpler expression strictly proportional to bisulfite gives $k_5 = (1.6 \pm 0.1) \times 10^5 \text{ M s}^{-1}$ with $R^2 = 0.33$.

We observe the O_2 and O_3 rate to be very nearly equal in neutral or weakly acidic solution. In clouds over the U.S. and Europe, with $\text{pH} \gtrsim 5$ and $\text{O}_3 \gtrsim 50 \text{ ppb}$, the O_3 reaction should be important.

1. INTRODUCTION

Sulfuric acid and its neutralization products with ammonia [H_2SO_4 , NH_4HSO_4 , $(\text{NH}_4)_2\text{SO}_4$] are important chemical components of the submicrometer-diameter particles suspended in the regional air masses covering Europe and the eastern U.S. (Charlson *et al.*, 1974; Brosset *et al.*, 1975; Cunningham and Johnson, 1976). These anthropogenic acid sulfate particles, produced by the oxidation of sulfur dioxide (SO_2), degrade visibility (Waggoner *et al.*, 1976), acidify rainwater (Bolin *et al.*, 1971; Likens and Bormann, 1974), and perhaps affect human health (Amdur *et al.*, 1975; Alarie *et al.*, 1975; Fairchild *et*

al., 1975). Several rate processes affect SO_2 oxidation in the atmosphere to produce these particles (Harrison *et al.*, 1976). We have re-examined two of these, namely the uncatalysed oxidation of SO_2 by oxygen (O_2) and by ozone (O_3) in aqueous solution. Various researchers have reported rate expressions for the uncatalysed O_2 reaction (Reinders and Vles, 1925; Fuller and Christ, 1941; Winkelmann, 1955; Schroeter, 1963; Beilke *et al.*, 1975) which result in at least order-of-magnitude uncertainty in this oxidation rate at pH values typical of atmospheric hydrometeors (4–6). For the analogous O_3 reaction, only one rate expression has previously been reported (Penkett, 1972). We present new measurements of the pH, temperature and oxidant partial pressure dependences of the uncatalyzed SO_2 oxidation rate by O_2 and by O_3 .

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II. EXPERIMENTAL PROCEDURE

A. Oxygen

Figure 1 shows a schematic diagram of the very simple apparatus used to study the O_2 reaction. To achieve reproducible results, the reaction system must be kept very clean and free of organic contaminants. Therefore solvent water was prepared by exposing de-ionized and then distilled water, with ~ 0.1 ml of 30% H_2O_2 added per liter, to intense u.v. (200–440 nm) radiation from a 1200 W mercury arc lamp for 2–3 h. This method is described by Armstrong and co-workers (1966) and has been shown by Williams (1969) to be at least as effective in removing organic carbon as triple distillation in potassium persulfate. Less than $\sim 5 \times 10^{-7}$ mol H_2O_2 l $^{-1}$ survived irradiation, as determined by the neutral buffered potassium iodide method (American Public Health Association, 1972).

Before each series of tests, the reaction vessel, a 300 ml Berzelius beaker, was cleaned in hot chromic acid for about 2 h and then rinsed in de-ionized, distilled water with a final rinse in irradiated water. Oxidation rates in a similarly cleaned polyethylene beaker were identical to those measured in glass, which we take as discounting the possibility of Cr^{6+} adsorption on the glass interfering with the reaction. The glass frit dispersion tube used to bubble oxygen through the solution and the Teflon coated magnetic stirring bar were also cleaned daily by irradiation. Finally, the O_2 (Airco medical grade) and nitrogen (N_2) (Matheson "pre-pure" 99.998%) mixture bubbled through the reaction vessel was pre-cleaned by passage through four glass gas washing bottles in series, containing, successively, 0.1 M sodium hydroxide, 0.1 M sulfuric acid, de-ionized distilled water, and irradiated water. Reaction temperatures of 278 ± 2 K were established by pre-cooling the irradiated water and by keeping the reaction vessel in an ice bath.

Sodium sulfite (Na_2SO_3) was recrystallized by the method of Johnstone (1946). 150 mg of the resultant recrystallized Na_2SO_3 was added to 150 ml of the O_2 saturated, cleaned water buffered at the desired pH by a series of buffers we shall describe in a later paragraph. The reacting solutions were vigorously stirred by the air flow (1.0–3.5 l min $^{-1}$) and by a magnetically driven Teflon stirring bar. Five ml aliquots were taken at measured times with an automatic pipette whose glass tip was also cleaned daily by irradiation. The concentration of sulfite in the diluted aliquot was then measured by iodimetric titration with sodium thiosulfate. This analytical method was found to be more accurate and reproducible than either turbidimetric sulfate analysis or manometric O_2 uptake analysis. However, comparison of the turbidimetric and iodimetric methods confirmed that for the unbuffered reaction the rate of sulfate production equalled the rate of sulfur (IV) ($SO_2 \cdot xH_2O$, HSO_3^- , SO_3^{2-} , $S_2O_5^{2-}$) decrease, within an ex-

perimental error of about 10% for the turbidimetric method and about 5% for the iodimetric method, with control Na_2SO_4 and Na_2SO_3 concentrations ranging from 100 to 1000 mg l $^{-1}$.

We also examined the effect of O_2 mass transfer on the oxidation rate of unbuffered sulfite solutions ($8.8 \leq pH \leq 9.8$). At a stirring speed of 100 rev/min, the apparent oxidation rate was not influenced by a total O_2 flow rate ranging from 0.1 to 7.0 l min $^{-1}$. The reactions were therefore run at about 3.1 l min $^{-1}$ total flow with O_2 partial pressures ranging from 0.11 to 1.0 atm, diluted to 1 atm total pressure with N_2 .

While oxidation at higher pH values requires consideration of mass transfer of O_2 into the solution, oxidation at lower pH values (≤ 5) requires consideration of mass transfer of SO_2 out of the solution. For this latter reason, the downstream concentration of SO_2 in air, bubbled through a solution of 6×10^{-5} M $NaHSO_3$ buffered at pH = 4.4, was measured with a flame photometer (Meloy Labs model SA-120). An SO_2 concentration of 1.25 ppmv was observed in downstream air that had been diluted 5 to 1 with clean air. This corresponds to a degassing rate of 14.7% h $^{-1}$, which may be compared to a theoretical rate of 16.3% h $^{-1}$, assuming an activity coefficient of 0.705 for HSO_3^- at the buffer concentration of 0.1 M (Ratkowsky and McCarthy, 1962). These rates are in good agreement and correspond to about 20% of the total rate of disappearance of sulfur (IV) from solution at this pH.

The effect of pH on the reaction rate was further studied using a variety of buffers at 0.1 M: for $4.3 < pH < 6$, we used sodium citrate and citric acid; for $6 < pH < 8$, we used potassium acid phosphate and sodium hydroxide; for $8 < pH < 10.5$, we used boric acid and sodium hydroxide; for $pH \geq 10.5$, we used sodium hydroxide. The effect of each of these buffers on the reaction rate was not detectable; first, varying the concentration of the buffer solutions by a factor of 10, from 0.1 to 1.0 M, did not affect the reaction rate; second, the rate of oxidation of the unbuffered solution did not differ from the observed rates in the boric acid-sodium hydroxide buffer at approximately the same pH.

B. Ozone

Figure 2 shows a schematic diagram of the apparatus used to study the O_3 reaction. To work with low concentrations of O_3 in air (sub-ppmv levels), the rate of contact of oxidant gas per mole of sulfur (IV) in solution must be increased. In the oxygen experiments the ratio of the rate of delivery of oxidant gas to the solution to the rate of oxidation of sulfur (IV) was at least equal to $\sim 10^2$ on a molar basis. Using O_3 , a value of four was achieved by using much smaller solution volumes, about 20 ml, at only a slightly lower gas flow rate, about 1.7 l min $^{-1}$, and a much lower initial sulfur (IV) concentration in solution,

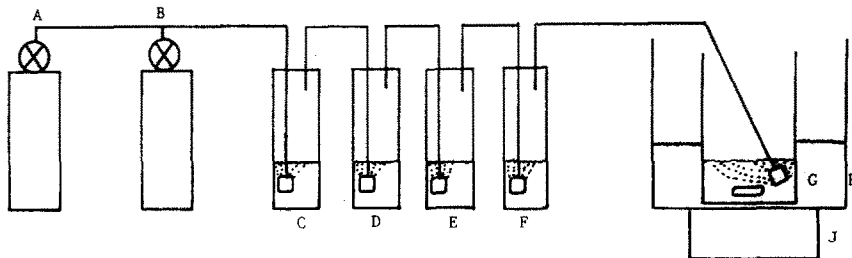


Fig. 1. Schematic diagram of sulfur dioxide oxygen kinetic experiment. A Metered oxygen, B metered nitrogen, C 0.1 M sodium hydroxide bubbler, D 0.1 M sulfuric acid bubbler, E deionized, distilled water, F irradiated water, G reaction beaker with dispersion tube and Teflon stirring bar, H water/ice bath, J magnetic stirrer.

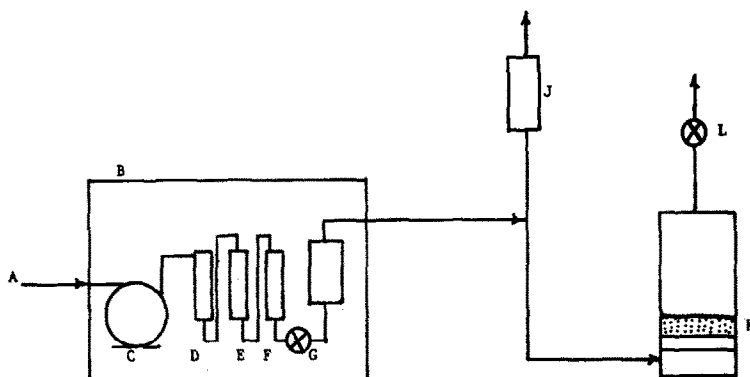


Fig. 2. Schematic diagram of sulfur dioxide ozone kinetic experiment. A Air inlet, B ozone generator, C pump, D charcoal filter, E soda lime filter, F chromate filter, G flow control valve, H u.v. exposure chamber (Teflon), J exhaust flowmeter, K reaction vessel, L vacuum valve.

about 10^{-5} M. Decreasing this ratio by a factor of two by further increasing the initial concentration of sulfur (IV) did not noticeably affect the oxidation rate at $\text{pH} = 4.5$. This demonstrated that the rate of O_3 delivery to the solution was large enough to eliminate mass transfer effects.

O_3 was produced by a commercially available ozone generator (Monitor Labs Model 8500) which uses an u.v. light source. This instrument was calibrated by the neutral buffered potassium iodide method (American Public Health Association, 1972) at each of three lamp current levels corresponding to 0.28, 0.60 and 0.95 ppmv O_3 respectively at 2.51 min^{-1} total flow. The use of smaller reaction volumes required changing the reaction vessel to a 150 ml gas washing bottle to allow more intimate contact of gas and liquid. The use of lower initial sulfur (IV) concentrations required adopting the more sensitive West-Gaeke (1956) colorimetric method for quantitative analysis. This method does not suffer from O_3 interferences at the concentrations we used. The experimental procedure was as follows:

A solution of 10^{-3} M NaHSO_3 at $\text{pH} = 3.5$ (to prevent rapid oxidation by O_2) was prepared fresh daily using sodium citrate-citric acid buffer and recrystallized Na_2SO_3 . Before each test, this solution was then diluted to 10^{-5} M. Twenty ml of this diluted solution was immediately added to the reaction vessel and 3 ml aliquots were taken at specified time intervals (usually every 5 to 10 min). These aliquots were mixed in test tubes with 1.0 ml of sodium tetrachloromercurate. Then 0.3 ml of formaldehyde and 0.3 ml pararosaniline-HCl were added to the test tubes and the color was allowed to develop for 24 h before the absorbance at 565 nm was measured.

III. RESULTS

A. Oxygen

The O_2 data consist of 94 runs with an average of five measurements per run for $\text{pH} \geq 5$, and 10 for $\text{pH} \leq 5$, covering a range of temperatures from 4 to 25°C , O_2 partial pressures from 0.11 to 1.0 atm, and pH values from 4.3 to 12.0. In most cases, the reaction was followed to at least 80% of completion. For the unbuffered runs at $T = 298 \text{ K}$, $\Delta t = 1 \text{ min}$; at $T = 278 \text{ K}$, Δt varied between 8 and 20 min. For the buffered data at both temperatures, $\Delta t = 0.2 \text{ min}$ for $\text{pH} \geq 9.5$; $\Delta t = 1-2 \text{ min}$ for $9.5 \geq \text{pH} \geq 6.5$;

$\Delta t = 6 \text{ min}$ for $6.5 \geq \text{pH} \geq 5$; and $\Delta t = 10-20 \text{ min}$ for $\text{pH} \leq 5$. The concentration vs time data for both the O_2 and O_3 reactions is tabulated in one of the author's dissertations (Larson, 1977). We have chosen to express these O_2 rate data in terms of the characteristic time with respect to sulfite ion, defined as:

$$\tau_{\text{SO}_3} = \left\{ -\frac{1}{[\text{SO}_3^{2-}]} \frac{d[R_s]}{dt} \right\}^{-1},$$

where $[\text{SO}_3^{2-}]$ is arithmetic mean concentration of sulfite ion in time interval t_2-t_1 , $[R_s]_i$ is sulfur (IV) concentration at time t_i adjusted for the amount of SO_2 degassed from the solution, and

$$-\frac{d[R_s]}{dt} \cong -\frac{\Delta[R_s]}{\Delta t} = \frac{[R_s]_1 - [R_s]_2}{t_2 - t_1}.$$

The concentration of sulfite ion was determined from $[R_s]$, the sulfite equilibria, and $[\text{H}^+]$, where $[\text{H}^+]$ was measured for the buffered runs and computed for the unbuffered runs from the relation:

$$[\text{H}^+] \cong \left\{ \frac{K_w K_{2s}}{[R_s]} \right\}^{1/2},$$

where K_w is the dissociation constant for water ($=1.008 \times 10^{-14} \text{ mol l}^{-1}$ at 25°C), K_{2s} is the second dissociation constant for dissolved SO_2 ($=6.24 \times 10^{-8} \text{ mol l}^{-1}$ at 25°C).

This approximation applies when $[\text{H}^+] < K_{2s} < [R_s]$ and is derived simply from a mass balance for sulfur (IV) and a charge balance for the $\text{Na}_2\text{SO}_3/\text{Na}_2\text{SO}_4$ solution.

The characteristic time for sulfite-ion oxidation is plotted vs solution pH in Figs. 3-6 for two different temperatures and for the buffered and unbuffered solutions.

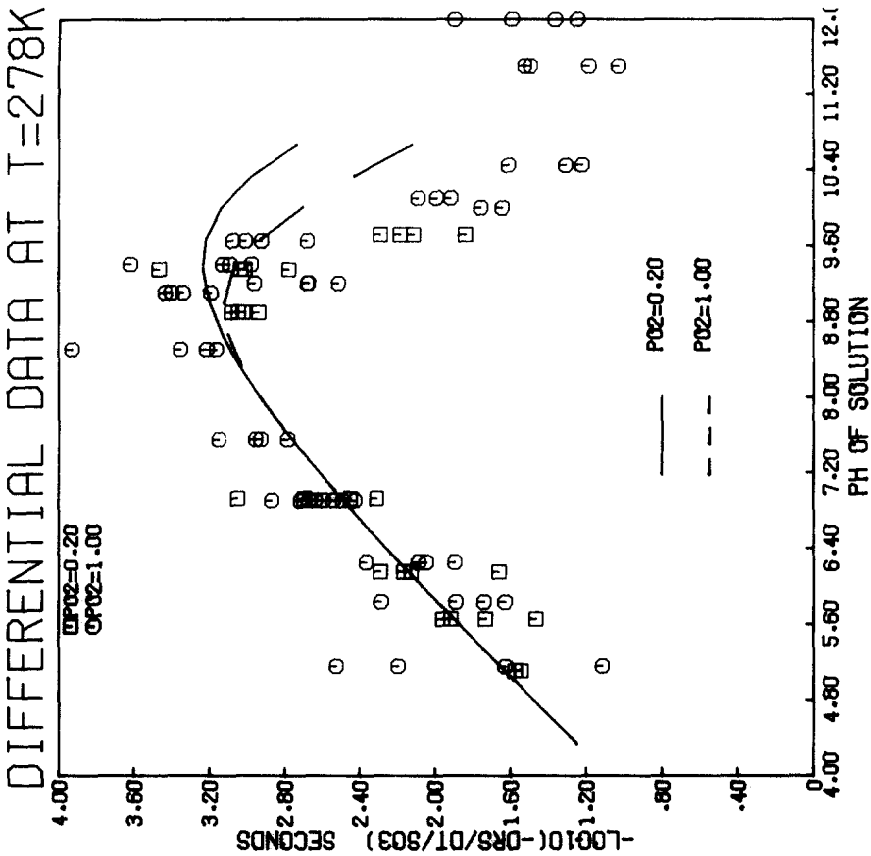


Fig. 4. Log log plot of characteristic oxidation time with respect to sulfite-ion concentration vs hydrogen-ion concentration for buffered solutions at two oxygen partial pressures at a reduced temperature of 278 K.

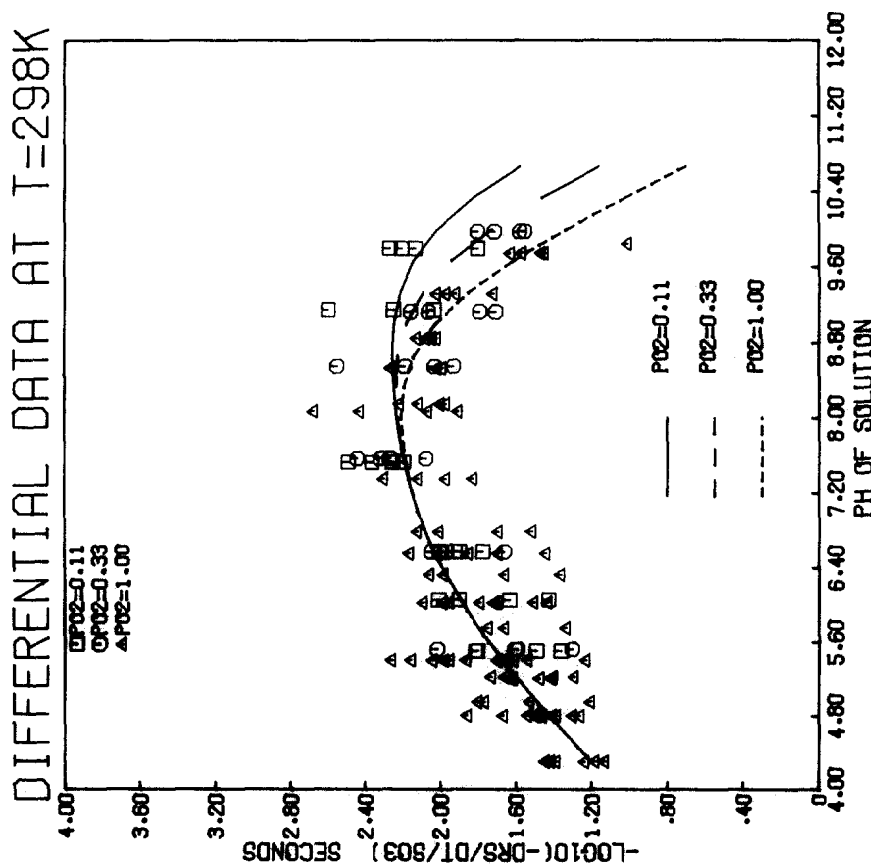


Fig. 3. Log log plot of characteristic oxidation time with respect to sulfite-ion concentration vs hydrogen-ion concentration for buffered solutions at three oxygen partial pressures at 298 K.

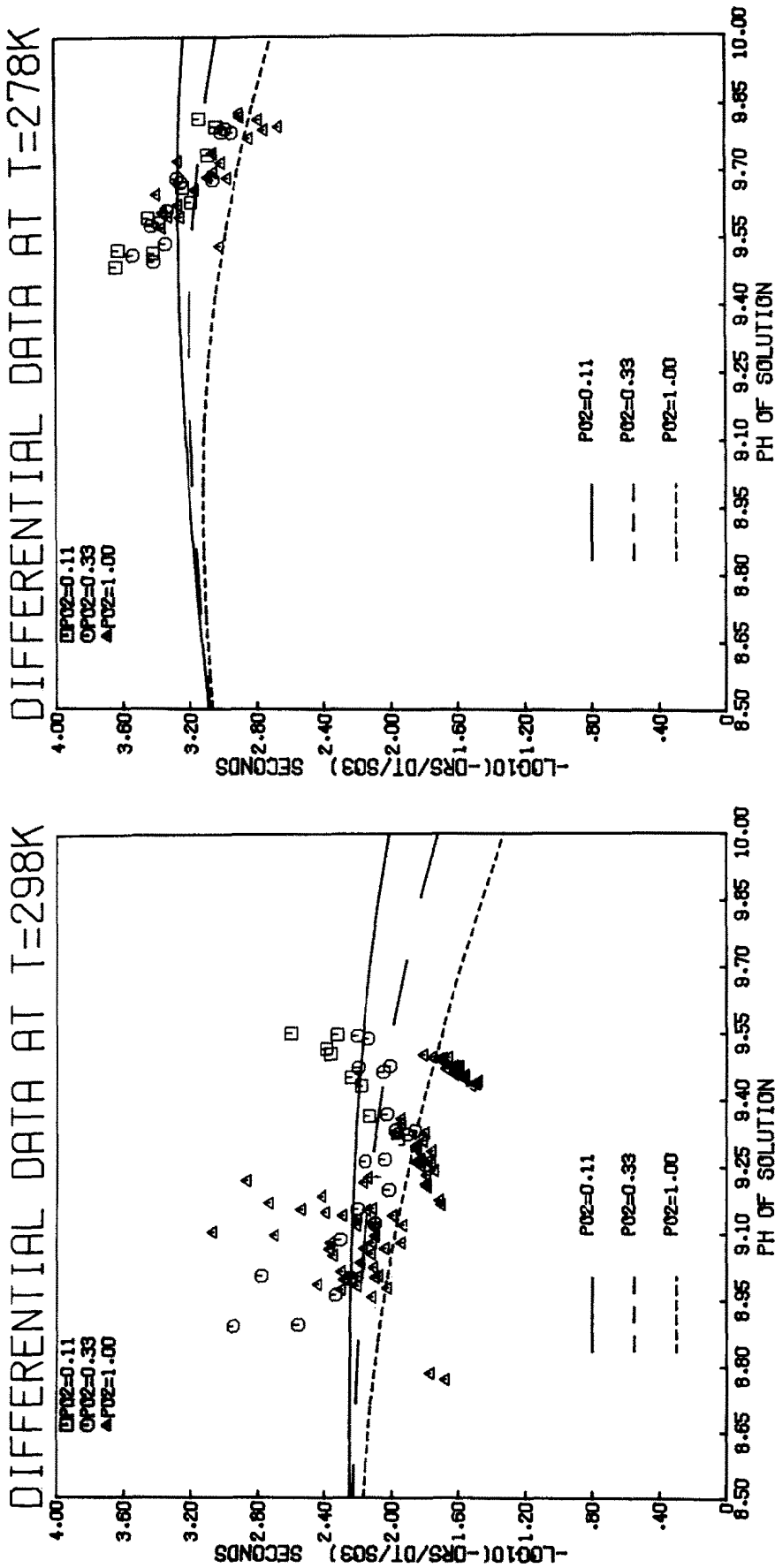


Fig. 5. Log-log plot of characteristic oxidation time with respect to sulfite-ion concentration vs hydrogen-ion concentration for unbuffered solutions at three oxygen partial pressures at 298 K.

Fig. 6. Log-log plot of characteristic oxidation time with respect to sulfite-ion concentration vs hydrogen-ion concentration for unbuffered solutions at three oxygen partial pressures at a reduced temperature of 278 K.

Since there is about a 5% measurement uncertainty in $[R_s]$, the relative error in $\Delta[R_s]/\Delta t$ and thus in τ_{SO_3} can be large, especially for small values of $\Delta[R_s]$. For $[R_s]_2/[R_s]_1 = 0.9$ and for an uncertainty = 0.05 $[R_s]$, the relative error in $\Delta[R_s] \cong 70\%$. This uncertainty in $\Delta[R_s]$ accounts for about one third of the scatter we observe, the remainder we attribute to fluctuations in residual solution impurities of both positive (metal ion) and negative (organic) catalysts. Although differentiating the data does add some apparent scatter, we chose this format because it makes no *a priori* assumptions about the rate expression and thus maximizes the number of degrees of freedom available for fitting a rate expression. Scatter of this magnitude is also reported and discussed by other researchers (e.g. Beilke *et al.*, 1975; Schroeter, 1963).

If the oxidation rate had been strictly proportional to the concentration of sulfite ion, the data plotted in Figs. 3–6 would have fallen on horizontal lines whose intercepts would determine a first-order rate constant. As can be seen in these plots, the data do not fall on horizontal straight lines. This deviation is also apparent from an integral analysis. Assuming a rate proportional to sulfite for the unbuffered runs (i.e. proportional to $[R_s][H^+]^{-2}$), integral plots of $[R_s]^{-1}$ vs time show slight negative curvature that can be accounted for by assuming an additional $[H^+]^{-1}$ dependence. This curvature is not apparent in the buffered runs ($\ln([R_s]_0/[R_s])$ vs t), implying that the oxidation rate is first order in $[R_s]$. From inspection of the buffered data at both temperatures (Figs. 3 and 4) and from consideration of previously reported expressions (Fuller and Christ, 1941; Schroeter, 1963), we have chosen an additional $[H^+]^{1/2}$ dependence in acid solutions. Therefore the curved lines shown in Figs. 3–6 are the fitted rate expression:

$$\frac{1}{[SO_3^{2-}]} \frac{d[R_s]}{dt} = k_1 + k_2[H^+]^{1/2} + k_3[H^+]^{-1}P_{O_2},$$

where P_{O_2} = partial pressure of O_2 (atm) and

$$k_i = k_i(298 \text{ K}) \exp \left\{ \frac{\Delta H_i}{R} \left(\frac{1}{298} - \frac{1}{T_i} \right) \right\}.$$

The k_i (298 K) are:

$$k_1 = (4.8 \pm 0.6) \times 10^{-3} \text{ s}^{-1}$$

$$k_2 = (8.9 \pm 1.0) \text{ s}^{-1} \text{ M}^{-1/2}$$

$$k_3 = (3.9 \pm 0.6) \times 10^{-12} \text{ s}^{-1} \text{ M atm}^{-1}$$

and

$$\Delta H_1 = (21.3 \pm 2.4) \text{ kcal mol}^{-1}$$

$$\Delta H_2 = (1.7 \pm 1.4) \text{ kcal mol}^{-1}$$

$$\Delta H_3 = (24.5 \pm 1.8) \text{ kcal mol}^{-1}.$$

The multiple correlation coefficient for this expression (R^2) is 0.73. The largest off-diagonal elements

in the normalized covariance matrix ($\cong 0.65$) are between k_2 and ΔH_2 and between k_3 and ΔH_3 .

In Figs. 7–9, our rate expression is compared with those reported by Reinders and Vles (1925), Fuller and Christ (1941), Beilke *et al.* (1975), Van den Heuval and Mason (1963) and Schroeter (1963). A confidence interval is indicated by also plotting the curves 1 s.d. above and below our best fit line. The only other experimental data taken with buffered solutions are those of Reinders and Vles (1925) (plotted as individual data points in Fig. 7) and Beilke *et al.* (1975) (plotted as the reported rate expression in Fig. 8). The other rate expressions are extrapolated either from unbuffered data at high pH (Van den Heuval and Mason, 1963) or from initial rate data at low pH taken by adding acid to unbuffered solutions (Schroeter, 1963; Fuller and Christ, 1941). As seen in Fig. 8, there is a marked discrepancy between our pH dependence at low temperature and that of Beilke *et al.* (1975). However, the majority of the data plotted in Figs. 7–9 agree with our results to indicate a positive catalytic effect of hydrogen ion on the sulfite ion oxidation rate in acid solution. We also agree with Beilke and coworkers (1975) that the oxidation rate has a weak temperature dependence in acid solution. In mildly alkaline solutions ($7 \leq \text{pH} \leq 9.5$), our measured activation energy is close to that reported by Barron and O'Hearn (1966) in the same pH range. The observed effect of O_2 partial pressure at $\text{pH} \geq 9.5$ is consistent with the conclusions of Schroeter (1963), but inconsistent with the results of Winkelmann (1955) who found no systematic O_2 dependence for pH values ranging from 7.0 to 10.3.

In strongly alkaline solutions ($\text{pH} \geq 10$), our rate data and accompanying chemical measurements contribute evidence relevant to the oxidation mechanism. At the completion of the reaction for $\text{pH} > 10$, the solution containing oxidized Na_2SO_3 was itself an oxidizing agent converting iodide to iodine in the titration flasks. This effect was most pronounced at $\text{pH} \geq 12$. Suspecting the production of peroxyacids of sulfur, we followed the method of Mariano (1968) to determine their presence and concentration. We found an oxidizing species that was reduced by As^{3+} in strongly acid solution; we therefore believe this species is peroxymonosulfate (Caro's ion: SO_5^{2-}), but have no spectroscopic evidence to support our conclusion. Since the solution did not subsequently oxidize Ce^{4+} in acid solution nor Fe^{2+} under nitrogen, we also conclude that $\text{S}_2\text{O}_8^{2-}$ and H_2O_2 were not present. Figure 10 shows the mole fraction of oxidizing species to initial sulfur (IV) in the final solution, measured six or more characteristic oxidation times after the start of the reaction. The fraction approaches 10% (about 10^{-3} M) at $\text{pH} = 12$. Since Caro's ion is a strong oxidizing agent, its presence is consistent with our observations of an increase in the oxidation rate of reduced sulfur at $\text{pH} \geq 9.5$. Both Goodman and Robson (1963) and Ball and Edwards (1956) report a $\text{p}K_2$ value of 9.5 for the $\text{SO}_5^{2-}/\text{HSO}_5^-$ equi-

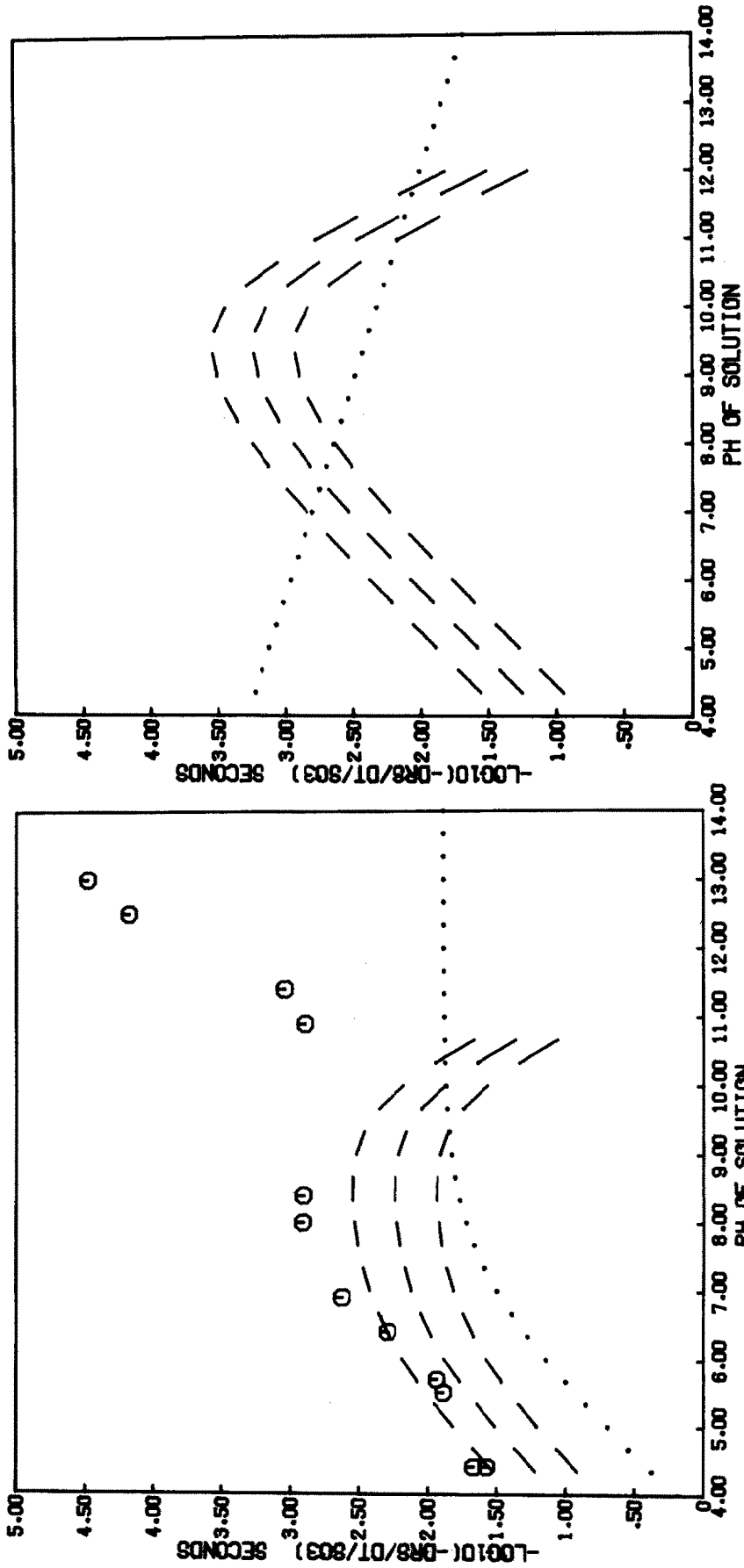


Fig. 7. Comparison of the characteristic time with respect to sulfite ion at 278 K predicted by our data (---, 1 s.d. above and below our best fit expression) with that predicted by the expression Beilke and coworkers (1975) (....).

Fig. 8. Comparison of the characteristic time with respect to sulfite ion at 298 K predicted by our data (---, 1 s.d. above and below our best fit expression) with that predicted by the data of Reinders and Vles (1925) (O) and the expression of Fuller and Christ (1941) (.....).

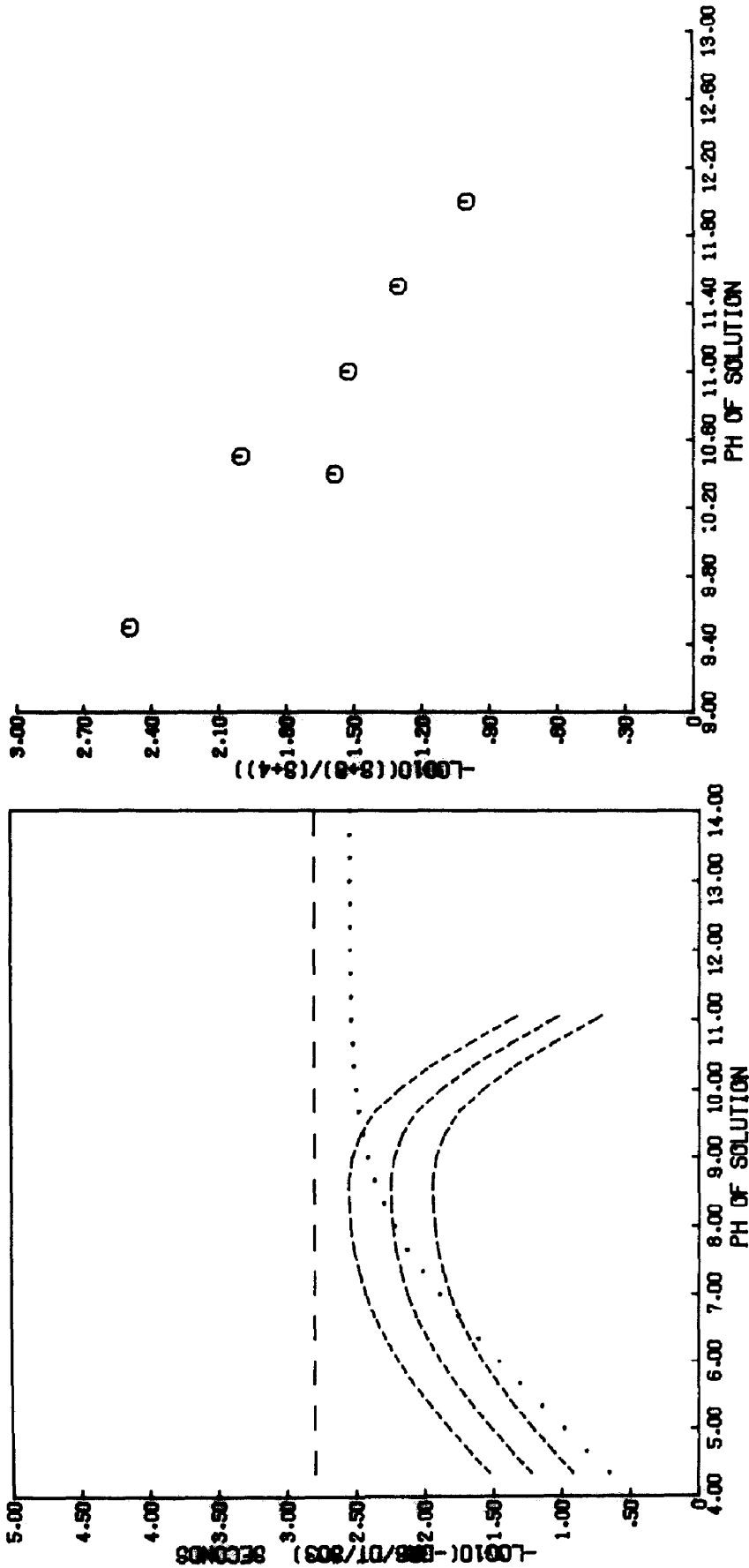


Fig. 10. Log log plot of the hydrogen-ion concentration vs the ratio of the concentration of sulfur (IV) initially in the solution before oxidation to the concentration of oxidizing species, found after six characteristic oxidation times.

Fig. 9. Comparison of the characteristic time with respect to sulfite ion at 298 K predicted by our data (—), 1 s.d. above and below our best fit expression) with that predicted by the expression of Van den Heuvel and Mason (1963) as interpreted by Scott and Hobbs (1967) (---) and by the expression Schroeter (1963) (....).

brium, which is the pH at which our rate begins to increase dramatically.

This alkaline region with increasing rates differs markedly from the kinetic data of Reinders and Vles (see Fig. 7) who used a manometric method to follow the reaction. To explore this discrepancy, we used a similar manometric method and also observed a slowing down of the rate of O_2 uptake for $pH \geq 9.5$. Further, we measured with a membrane probe (Yellow Springs Instrument Model 54) the dissolved O_2 in the closed vessel, while simultaneously measuring the O_2 pressure above the solution. At $pH = 9$, the dissolved O_2 was rapidly depleted upon dissolution of the Na_2SO_3 , and the pressure above the solution decreased at a relatively rapid rate. However, at $pH = 12.5$, while the dissolved O_2 was again rapidly depleted, the pressure above the solution decreased at a very much slower rate until it reached the same final value that it had at $pH = 9$. The temperature of the solution in both cases was $21.5^\circ C$. Continuing this exploration, we also measured the rate of sulfate production turbidimetrically at $pH = 12.5$ in an open reaction vessel (taking care during the analyses to adjust the pH of the samples to 2.5 with HCl before adding $BaCl_2$). At pH 12.5, when O_2 was added by

simply stirring the solution in an open vessel, the rate slowed. Upon vigorous injection of air into the solution by bubbling through a glass frit, the rate showed a dramatic increase, implying that the O_2 mass transfer rate into the solution had decreased at high pH. From these tests we conclude that the apparent slowing of the oxidation rate at high pH observed by Reinders and Vles (1925) was influenced by mass transfer.

B. Ozone

The O_3 kinetic data consist of 29 runs with an average of five measurements per run covering a range of temperature from 5 to $25^\circ C$, O_3 partial pressure from 2.8×10^{-7} to 9.5×10^{-7} atm, and pH from 4.0 to 6.2. For most runs, Δt varied between 3 and 5 min. We have chosen to present the resulting differential O_3 data in terms of the characteristic time with respect to bisulfite ion, defined as:

$$\tau_{HSO_3} = \left\{ - \frac{1}{[HSO_3^-]} \frac{d[R_s]}{dt} \right\}^{-1},$$

where $[HSO_3^-]$ is the arithmetic mean concentration of bisulfite ion in the time interval $t_2 - t_1$. This charac-

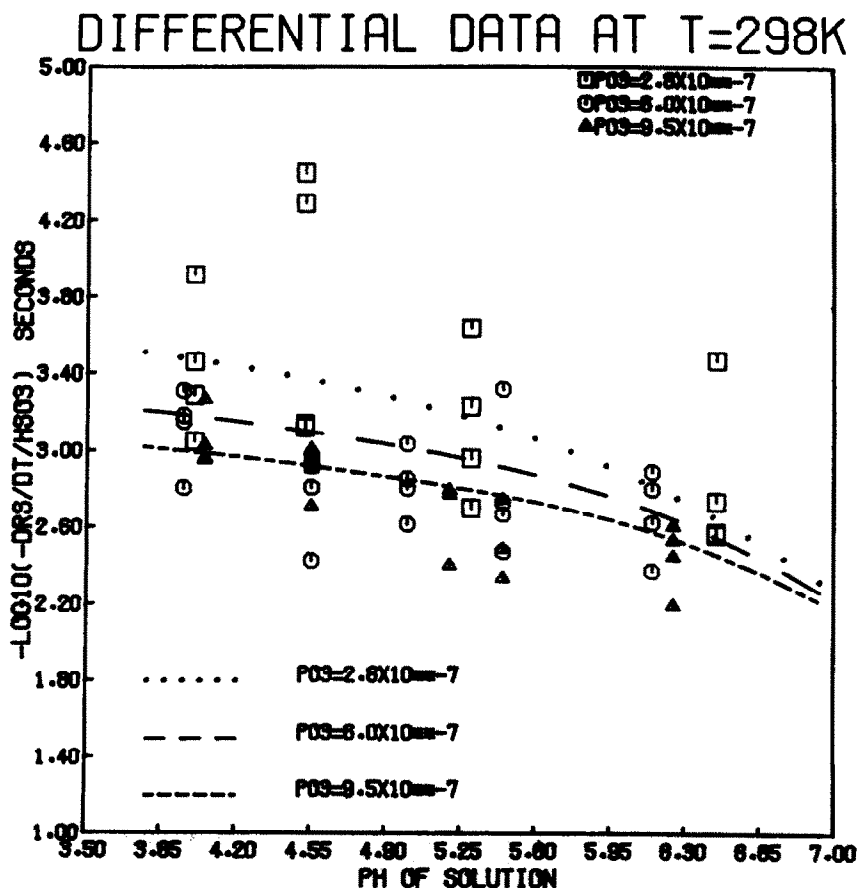


Fig. 11. Log-log plot of the hydrogen-ion concentration vs the characteristic time with respect to the bisulfite-ion concentration at 298 K for three ozone partial pressures. Lines drawn through the data are our best fit rate expression [proportional to $P_{O_3} (HSO_3^-) (H^+)^{-0.1}$].

teristic time is plotted in Figs. 11 and 12 for two different temperatures. If the O_3 oxidation rate had been strictly proportional to the concentration of bisulfite ion, the data would not have fallen on a horizontal line. This is because, for these O_3 concentrations, the O_2 reaction rate becomes competitive for $pH \geq 5.5$ and this rate is not proportional to bisulfite ion. This effect is seen in both Figs. 11 and 12, where the best fit rate expression plotted with the data displays some curvature at the higher pH values. This best-fit ($R^2 = 0.38$) three parameter rate expression is:

$$\frac{-d[R_s]}{dt} = k_4 P_{O_3} K_{HO_3} [HSO_3^-] [H^+]^{k_5} + [SO_3^{2-}] \{k_1 + k_2 [H^+]^{1/2}\},$$

where

k_4 is $(4.4 \pm 2.0) \times 10^4 \text{ M}^{-0.9} \text{ s}^{-1}$ at 298 K, ΔH_4 is $3.9 \pm 1.0 \text{ kcal mole}^{-1}$, P_{O_3} is partial pressure of ozone (atm), K_{HO_3} is Henry's law constant for ozone = $0.0123 \text{ M atm}^{-1}$ at 298 K.

$$\Delta H_{HO_3} = -4.0 \text{ kcal M}^{-1}$$

$$k_5 = -0.1 \pm 0.03.$$

A four-parameter expression was initially fit to the O_3 data, namely:

$$\begin{aligned} -\frac{d[R_s]}{dt} = & X_1 (K_{HO_3} P_{O_3})^{X_2} [HSO_3^-] [H^+]^{X_3} \\ & \times \exp \left[\frac{-X_4}{R} \left(\frac{1}{298} - \frac{1}{T} \right) \right] \\ & + [SO_3^{2-}] \{k_1 + k_2 [H^+]^{1/2}\}, \end{aligned}$$

where the X_i are the predictor variables. However, owing to the strong correlation between X_1 and X_2 (a covariance = 1.00), the minimization routine was unable to find a minimum in the sum of squares of residuals. The solution stabilized with $X_2 = 0.92 \pm 0.16$ and with $R^2 = 0.36$. Therefore X_2 was eliminated as a variable by assuming that the rate was first order with respect to O_3 , as Penkett (1972) had found. The three-parameter model was then used in the minimization routine and a minimum was found. For comparison, we also fitted Penkett's expression with an added temperature dependence:

$$\frac{-d[R_s]}{dt} = k_6 [HSO_3^-] K_{HO_3} P_{O_3} - \frac{d[R_s]}{dt}_{\text{oxygen}}$$

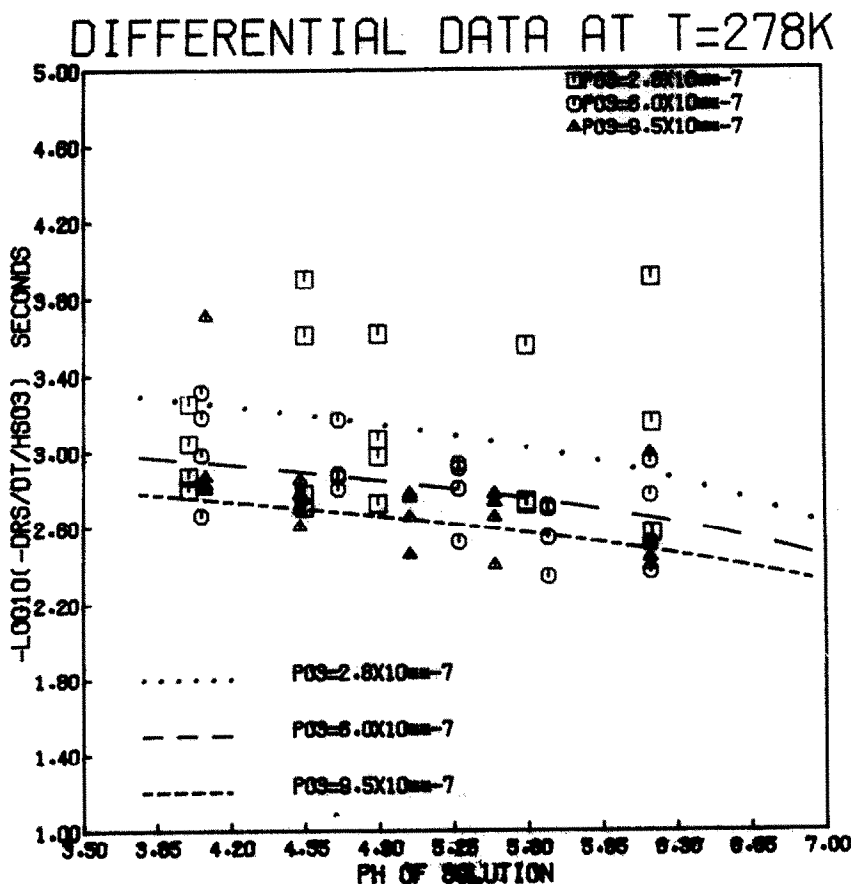


Fig. 12. Log-log plot of the hydrogen-ion concentration vs the characteristic time with respect to the bisulfite-ion concentration at a reduced temperature of 278 K for three ozone partial pressures. Lines drawn through the data are our best fit rate expression [proportional to $P_{O_3} (HSO_3^-) (H^+)^{-0.1}$].

to the data and found that:

$$k_6 = (1.6 \pm 0.1) \times 10^5 \text{ M}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

$$\Delta H_6 = 3.8 \pm 1.1 \text{ kcal mol}^{-1},$$

with $R^2 = 0.33$ which is about one half the value for k_6 obtained by Penkett. This simpler expression describes our data almost as well as the three-parameter expression.

We have compared our data with Penkett's expression in Fig. 13. Although some of the discrepancy is due to scatter in the data, not all of it is. However, Penkett's experiments involved measuring O_3 depletion in the presence of excess bisulfite at O_3 concentrations about 1000 times greater than ours. Therefore, a discrepancy is not surprising. If we were to increase our O_3 concentrations by 1000 and were able to measure the reaction rate, we would arrive at Penkett's rate if the order with respect to O_3 concentration were about 1.10, assuming that the pH dependence of the reaction rate does not change with changing O_3 concentrations. This gives additional support to our assumption of a first order O_3 dependence.

Although Penkett's measurements do not agree

precisely with ours, we both conclude that with $p\text{O}_3 \approx 10^{-6}$ atm the O_3 reaction is significantly faster than the O_2 reaction ($p\text{O}_2 = 0.2$ atm) for pH values less than 5.6, the equilibrium value for the atmospheric CO_2 buffer. This fact is displayed in Fig. 14, where our O_3 and O_2 expressions are compared over the pH range from 3.5 to 7.0. Penkett's expression would predict an even greater difference beginning at a higher pH.

Another important feature of the O_3 reaction is shown in Fig. 14. With increasing pH and therefore increasing $\text{SO}_3^{2-}/\text{HSO}_3^-$ ratios, the O_3 rate remains nearly constant, but the O_2 rate increases (time decreases). This indicates that the O_2 reacts preferentially with unprotonated sulfur species (SO_3^{2-} , SO_3^-), whereas the O_3 does not. In fact, the slope of the plots in Fig. 14 can be considered a measure of the preference of the oxidant for reaction with protonated versus unprotonated sulfur species in solution. Therefore in the presence of both O_2 and O_3 , for $\text{pH} \leq \text{p}K_{2s}$, decreasing the pH protonates the dissolved sulfur species and decreases the O_2 to O_3 rate ratio. Similarly, for $\text{pH} \geq \text{p}K_{2s}$, the O_2 reaction appears to be dominant if $p\text{O}_3 \leq 10^{-6}$ atm.

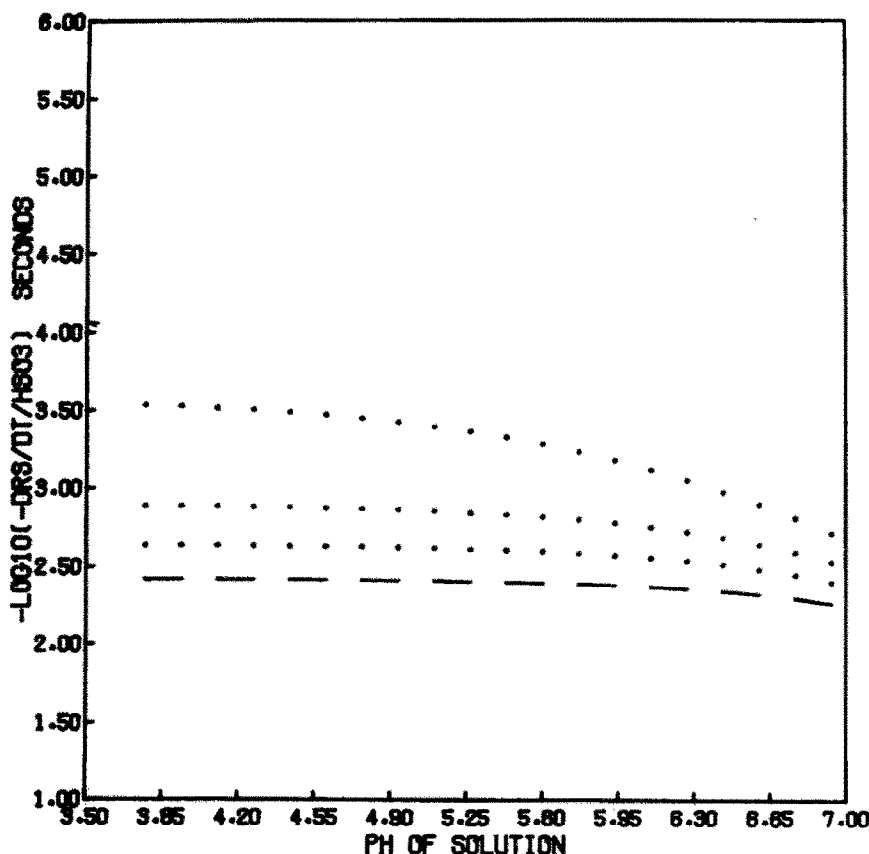


Fig. 13. Comparison of the characteristic time with respect to bisulfite-ion concentration at 283 K predicted by our rate expression (....., 1 s.d. above and below our best fit expression) with that predicted by Penkett's expression (---). $\text{O}_3 = 0.6$ ppmv.

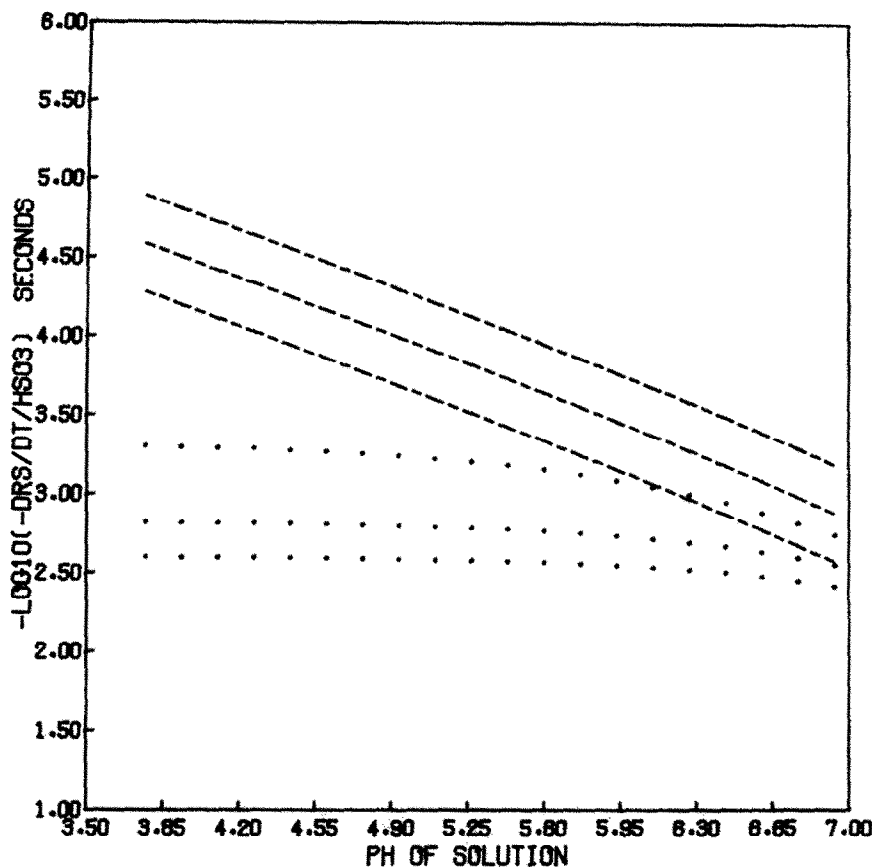


Fig. 14. Comparison of the characteristic time with respect to bisulfite-ion concentration at 278 K predicted by our ozone-rate expression (---) with that predicted by our oxygen-rate expression (....). The two outside lines in each case represent 1 s.d. above and below the central line best fit expression. $O_3 = 0.6$ ppmv.

IV. DISCUSSION OF RESULTS

Our rate expressions for O_2 and O_3 provide insight into the respective reaction mechanisms, and allow us to predict the relative importance of these reactions in the production of atmospheric sulfate particles. We shall discuss the reaction mechanisms first, focussing mainly on the oxygen reaction. We shall then discuss the relevance of these reactions in terms of atmospheric SO_2 oxidation mechanisms, reserving a more detailed analysis of in-cloud oxidation rates to another paper.

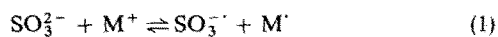
A. Reaction mechanisms

The O_2 reaction mechanism in acid and weakly alkaline solution has been the subject of much speculation by previous researchers. Of those free radical mechanisms discussed in the literature, Bäckström's (1934) mechanism seems to have received the most attention. Not only does it involve the $SO_3^{\cdot-}$ and $SO_5^{\cdot-}$ free radicals found by Hayon *et al.* (1972), but also it involves gaseous O_2 as the dominant source of oxygen atoms, without isotopic exchange with H_2O (Winter and Briscoe, 1951; Halperin and Taube,

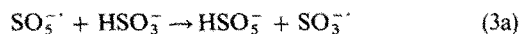
1952), produces a small amount of dithionate ($S_2O_6^{2-}$) as a side product (Bassett and Parker, 1951), and explains the oxidation of organic inhibitors (Alyea and Bäckström, 1929) and inorganic inhibitors such as As^{3+} (Jorissen, 1959).

In Bäckström's mechanism, $SO_3^{\cdot-}$ is the free radical chain carrier and metal ion initiates free radical formation:

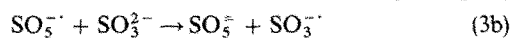
Chain initiation:



Propagation:

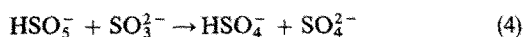


pH < pK_{2s}



pH > pK_{2s}

Oxidation:



Termination:

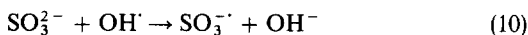
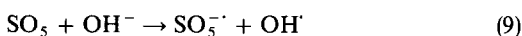
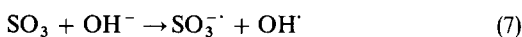
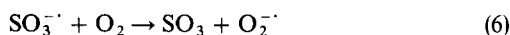


Setting the initiation and termination rates equal, assuming long chains ($k_5 \ll k_3$), and claiming step (2) is rate determining, we have at steady state:

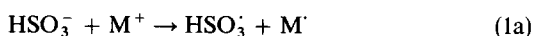
$$\frac{d[\text{SO}_4^{2-}]}{dt} = \left(\frac{k_1}{K_{2s}k_2k_5} \right)^{1/2} [\text{M}^+]^{1/2} [\text{O}_2]^{1/2} \times \{k_{3b}^{1/2} + k_{3a}^{1/2} [\text{H}^+]^{1/2}\} [\text{SO}_3^{2-}],$$

which has the pH dependence we have found for $\text{pH} \lesssim 9$. The simplicity of this mechanism is appealing; the dependence of the rate on $[\text{M}^+]^{1/2}$ can help to explain the scatter in our data. However, the $[\text{O}_2]^{1/2}$ dependence is not what we observe. Further, our observation of an acceleration in the rate for $\text{pH} \gtrsim 9$ is not explained by this mechanism, especially since $[\text{M}^+]$ would decrease due to metal hydroxide precipitation with increasing pH.

To respond to these criticisms, we propose a modification of Bäckström's mechanism. For $\text{pH} > \text{p}K_{2s}$, we replace step (2) with the sequence:



For $\text{pH} < \text{p}K_{2s}$, we replace the initiation step (1) with bisulfite:



where HSO_3^{\cdot} is in equilibrium with $\text{SO}_3^{\cdot-}$ so that

$$K_7 = \frac{[\text{SO}_3^{\cdot-}][\text{H}^+]}{[\text{HSO}_3^{\cdot}]}$$

with the following additional assumptions:

- (a) the rate determining step is reaction (6); and
- (b) $k_7 > k_8$,

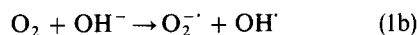
we can derive a steady-state rate expression with the observed pH and O_2 partial pressure dependences for $\text{pH} < 10$:

$$\begin{aligned} \frac{-d[R_s]}{dt} &= \frac{d[\text{SO}_4^{2-}]}{dt} \\ &= [\text{SO}_3^{2-}] [\text{M}^+]^{1/2} \left[\frac{k_3 k_6 k_7 K_w^{1/2}}{k_5 k_8 K_{2s}} \right] \\ &\quad \times \{k_1^{1/2} + k_{1a}^{1/2} [\text{H}^+]^{1/2}\}. \end{aligned}$$

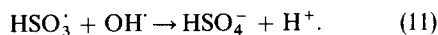
Adding the $\text{SO}_4^{\cdot-}$ sequence suggested by Hayon *et al.* (1972) does not affect this result.

At high pH (≥ 10), a viable mechanism might also include the production of Caro's ion, SO_3^{2-} , and perhaps $\text{O}_3^{\cdot-}$ as reported by Hayon *et al.* (1972). We can modify our acid mechanism to do this by replacing the O_2 initiation step (1) with one that includes hydroxide ion:

oxide ion:



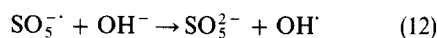
and replacing the termination step (5) with one that includes the newly produced OH^{\cdot} radical:



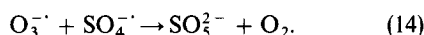
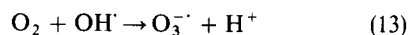
This revision results in the following rate expression:

$$\frac{d[\text{SO}_4^{2-}]}{dt} = [\text{SO}_3^{2-}] \left(\frac{k_6 k_{10} K_2}{k_{11}} \right) [\text{H}^+]^{-1} P_{\text{O}_2},$$

which has correct pH and O_2 dependences. Adding the additional propagation step:



predicts an increased production of SO_5^{2-} and OH^{\cdot} at high pH. Considering the mechanism of Hayon *et al.* (1972), we can also include an $\text{OH}^{\cdot}/\text{SO}_4^{\cdot-}$ sequence to produce $\text{O}_3^{\cdot-}$ and more SO_5^{2-} :



Since experimental constraints required that the O_3 rate measurements be taken over a fairly narrow pH range, compared to the O_2 measurements, it is more difficult to test a comprehensive O_3 reaction mechanism. Based on our experience with the O_2 reaction, it seems likely to us that the O_3 reaction mechanism involves free radicals and that the same sulfur radicals are involved in both reactions. Similar weak temperature dependences for both reactions in this pH range also suggest this similarity in the oxidation mechanism. In the O_3 reaction sequence, however, the rate-determining reaction step does not depend on the extent of protonation of the free radical. We suggest that further studies of the reaction mechanism be performed to include examination of inhibition, solvent oxygen exchange, free radical formation, and reaction side products analogous to the qualitative studies mentioned involving O_2 . To maximize reproducibility and minimize the contribution from simultaneous O_2 reactions, we also suggest that the O_3 partial pressure be $\geq 10^{-5}$ atm.

B. Significance to atmospheric processes

These rate expressions allow us to weigh the importance of the two reactions in the production of atmospheric sulfate particles. We conclude that the O_3 reaction is more important than the O_2 reaction for O_3 mixing ratios equal to or greater than 50 ppbv, which are typical of background levels in the Eastern U.S. (Westberg *et al.*, 1976; Chatfield and Harrison, 1976a, b, c), and for a solution pH less than about 5.5. Since rainwater pH in the eastern U.S. and in

Europe rarely exceeds 5.5 (Lodge *et al.*, 1968; Bolin *et al.*, 1971) less dilute atmospheric solutions (aerosol and cloud droplets) should be at least as acid. Only in the presence of either excess NH_3 or basic particulate compounds such as Na_2CO_3 and CaCO_3 would the pH exceed 5.5. Therefore the uncatalysed O_3 reaction would appear to dominate the O_2 reaction most of the time in these regions.

However, our recent measurements (Larson *et al.*, 1977) indicate that typical NH_3 concentrations in exhaled air from human subjects during quiet mouth breathing are several hundred ppbv. Therefore, for typical atmospheric SO_2 concentrations of 10–30 ppbv and a high SO_2 scrubbing efficiency in the nasal passages (Frank *et al.*, 1969), the pH of inhaled droplets can exceed 5.5 and the O_2 reaction would appear to dominate any SO_2 oxidation that occurs in the atmosphere of the lung.

Owing to the relatively small amount of liquid water involved, neither the O_2 or O_3 reaction is fast enough to produce significant quantities of sulfate in the liquid phase associated with a hygroscopic aerosols at humidities less than saturation. These reactions could only occur at a significant rate under saturated conditions, that is in fogs or clouds, where the liquid water content may exceed 0.1 g m^{-3} . We shall discuss this in-cloud oxidation chemistry in greater detail in another paper. For this present discussion, we can simply state that for an O_3 mixing fraction of 50 ppb, a liquid water content of 0.6 g M^{-3} , and initial SO_2 and NH_3 mixing fractions of 10 ppb, our measured O_3 rate predicts $10 \mu\text{g M}^{-3}$ of NH_4HSO_4 would be formed in 24 h with an accompanying $\text{SO}_2/\text{SO}_4^{2-}$ molar ratio of 5. These latter values are consistent with the atmospheric measurements cited earlier, and this production time is competitive with a homogeneous reaction rate in heavily polluted air of $1\text{--}4\% \text{ h}^{-1}$ (Harrison *et al.*, 1976; Calvert, 1973). In making these calculations, we have assumed that the air parcel does not exchange sulfur with its surroundings; that is, turbulent mixing with other air parcels of differing SO_2 or sulfate concentrations has been neglected. This assumption is most reasonable for the well-mixed boundary layer and least reasonable for near-source chemistry.

We have not as yet made similar computations using reported transition metal catalyzed rate expressions. However, these reactions seem to be more important near the source of SO_2 emission, because they are second order in sulfur (IV) concentration (Freiberg, 1974; Bracewell and Gall, 1967) and their reaction rates therefore decrease rapidly with atmospheric dispersion. These reactions also appear to display a preference for unprotonated sulfur species (Junge and Ryan, 1958) which would enhance quenching as acid sulfates are produced downwind. Whether the metal-ion catalysed O_3 reactions display either of these self-quenching features remains to be tested. Since this set of reactions could also be important in the atmosphere, we suggest that bulk phase kinetic experiments

be undertaken to measure metal ion, sulfur, pH, O_3 and temperature dependences.

V. SUMMARY

We have examined the kinetics of the uncatalyzed oxidation of SO_2 by O_2 and by O_3 . For the O_2 reaction, we have observed a positive effect of hydrogen ion on the rate of sulfite ion oxidation in acid solution similar to that found by other researchers (varying with $[\text{SO}_3^{2-}][\text{H}^+]^{1/2}$). We have also found a weak temperature dependence between 5 and 25°C . At 5°C , the temperature of a warm cloud, our measured O_2 rate is similar to the fastest of those rates quoted in previous cloud oxidation models (e.g. Easter and Hobbs, 1974). We have proposed a modification of Bäckstrom's (1934) free radical mechanism to explain the O_2 results. This mechanism is also consistent with more recent qualitative experiments and is able to explain the presence of strong oxidants which we believe are present at high pH (>10).

For the O_3 reaction at partial pressures near 10^{-6} atm, we have observed in acid solution an oxidation rate nearly proportional to bisulfite ion, similar to the results reported by Penkett (1972) at O_3 partial pressures three orders of magnitude larger. We have not found a measurable effect of temperature on this rate, analogous to the weak dependence of the O_2 reaction in acid solution. We conclude that the O_2 and O_3 rates are nearly equal in neutral or weakly acid solutions, but that the O_3 reaction dominates the O_2 reaction in clouds with $\text{pH} \leq 5$ at typical O_3 mixing fractions ≥ 50 ppbv.

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