

## ON THE KINETICS AND MECHANISM OF OXIDATION OF AQUATED SULFUR DIOXIDE BY OZONE

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(First received 27 March 1985 and in final form 5 November 1985)

**Abstract**—Kinetic data obtained from a number of different investigators on the reaction of S(IV) with ozone in aqueous solution have been analyzed in terms of a single self-consistent rate expression. The rate expression that most appropriately fits all kinetic observations treated in this study is:

$$-d[S(IV)]/dt = (k_0\alpha_0 + k_1\alpha_1 + k_2\alpha_2)[S(IV)][O_3]$$

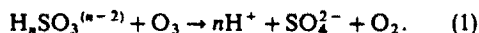
where  $\alpha_0$ ,  $\alpha_1$  and  $\alpha_2$  denote the fraction of S(IV) in the form of  $SO_2 \cdot H_2O$ ,  $HSO_3^-$  and  $SO_3^{2-}$ , respectively. This kinetic expression is similar in form to the empirical rate laws reported by Erickson *et al.* (1977, *Atmospheric Environment* 11, 813-817) and Hoigne *et al.* (1985, *Water Res.* 19, 993-1004). The recommended values for  $k_0$ ,  $k_1$  and  $k_2$  are  $(2.4 \pm 1.1) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ,  $(3.7 \pm 0.7) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , and  $(1.5 \pm 0.6) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. The activation energies that are recommended for  $k_1$  and  $k_2$  are taken from Erickson *et al.* (1977) as  $46.0 \text{ kJ mol}^{-1}$  and  $43.9 \text{ kJ mol}^{-1}$ , respectively. The reaction proceeds via three independent pathways that involve a nucleophilic attack on ozone by  $SO_3^{2-}$ ,  $HO-SO_2^-$ , and  $SO_2 \cdot H_2O$ . Rate laws and kinetic data of five investigators are compared for an open cloud water system with a liquid water content of  $0.2 \text{ gm}^{-3}$ .

### INTRODUCTION

Oxidation of  $SO_2$  by  $O_2$ ,  $O_3$ ,  $NO_2$  or  $H_2O_2$  in aqueous microdroplets or hydrometeors has been acknowledged as a viable non-photolytic pathway for the production of  $H_2SO_4$  in fogs, clouds and humid atmospheres (Hoffmann and Boyce, 1983; Hoffmann and Jacob, 1984; Jacob and Hoffmann, 1983). Oxidation by either  $O_3$ ,  $H_2O_2$ , or the combination of the two has been shown to be a particularly important S(IV)-conversion pathway in clouds and fogs (Jacob and Hoffmann, 1983; Martin, 1983, 1984; Hegg and Hobbs, 1982). Martin (1983) has recently analyzed data obtained by Hegg and Hobbs (1982) for the production of sulfate in wave clouds in terms of the known kinetics of  $O_3$  oxidation of sulfur (IV) (i.e. total aquated sulfur dioxide). He has shown that the observed transformation rates of Hegg and Hobbs can be interpreted quantitatively in terms of the kinetic data of Maahs (1983a, b). The correlation between predicted and observed sulfate production rates as a function of pH is reasonably high.

$O_3$  can be classified as a 'fast oxidant' of  $SO_2$  in the pH range  $\geq 4$  along with  $H_2O_2$  and nitrous acid (Martin, 1984). However the above oxidants are substantially less abundant than  $O_2$ , which is a competitive oxidant in aqueous solution (Hoffmann and Boyce, 1983; Hoffmann and Jacob, 1984; Boyce *et al.*, 1983). In spite of their lower gas-phase concentrations,  $H_2O_2$  and  $O_3$  have significantly higher Henry's Law Constants (Jacob and Hoffmann, 1983) than  $O_2$ . This feature combined with their unusual reactivity make them highly competent oxidants both thermodynamically and kinetically.

The kinetics of the reaction [Equation (1)] of sulfur (IV) and ozone have been studied by a number of investigators.



Penkett (1972), Penkett *et al.* (1979), Erickson *et al.* (1977), Larson *et al.* (1978), Harrison *et al.* (1982), Maahs (1983a, b), Hoigne *et al.* (1985) and Martin (1984) have studied the kinetics of this reaction over a broad pH range of  $-0.3$  to  $7.0$ . A summary of empirical rate laws and observed rate constants reported by these investigators is presented in Table 1. There appears to be reasonable agreement among the investigators in principle for the rate of the reaction over a limited pH range as determined by the cluster of observed rate constants in the range of  $10^4$ – $10^5 \text{ M}^{-1} \text{ s}^{-1}$ . However, there appears to be less agreement with respect to the overall kinetic order; in particular there is some disagreement as to the exact reaction order with respect to  $[H^+]$ . The work of Erickson *et al.* and Maahs and Hoigne *et al.* indicates that the overall rate of reaction is described by a multi-term rate law. Erickson *et al.* and Hoigne *et al.* have used basically the same three-term rate law to describe the kinetics over the pH range of  $-0.3$  to  $7.0$ . They have found that all three of the major S(IV) species,  $H_2O \cdot SO_2$ ,  $HSO_3^-$  and  $SO_3^{2-}$  react with  $O_3$  via separate kinetic pathways to give S(VI) and  $O_2$ . These investigators have reported individual second-order rate constants for each pathway. The work of Maahs is in general agreement with the results of Erickson *et al.* and Hoigne *et al.* He has interpreted his results primarily in terms of a single reactive S(IV) species,

Table 1. Empirical rate laws for the oxidation of S(IV) by ozone

| Rate ( $v = -d[S(IV)]/dt$ )                                       | Rate constants  | Conditions  | Reference                     |
|---|---|---|-------------------------------|
| $v = k_1[HSO_3^-][O_3] + k_2[SO_3^{2-}][O_3]$                     | $k_1 = 3.1 \times 10^5 M^{-1} s^{-1}$<br>$E_{a,1} = 46 kJ mol^{-1}$<br>$k_2 = 2.2 \times 10^9 M^{-1} s^{-1}$<br>$E_{a,2} = 43.9 kJ mol^{-1}$  | pH 0-4<br>$T = 25^\circ C$                              | Erickson <i>et al.</i> (1977) |
| $v = (k_0[H_2O \cdot SO_3] + k_1[HSO_3^-] + k_2[SO_3^{2-}])[O_3]$ | $k_0 = (2 \pm 2) \times 10^4 M^{-1} s^{-1}$<br>$k_1 = (3.2 \pm 0.2) \times 10^5 M^{-1} s^{-1}$<br>$k_2 = (1.0 \pm 0.2) \times 10^9 M^{-1} s^{-1}$   | pH 1-6<br>$T = 22^\circ C$                              | Hoigne <i>et al.</i> (1985)   |
| $v = (k_1 + k_2[H^+]^{-1})[S(IV)][O_3]$                           | $k_1 = 4.39 \times 10^{11} e^{-4131/T} (\pm 3 \times 10^4) M^{-1} s^{-1}$<br>$k_2 = 2.56 \times 10^3 e^{-966/T} (\pm 15) s^{-1}$<br>$\log k = \log k_0 + (\sqrt{\mu}/(1 + \sqrt{\mu})) - 0.3\mu$<br>$k = 1.9 \times 10^4 M^{-0.5} s^{-1}$ | pH 3-6.2<br>$T = 10-25^\circ C$<br>$\mu = 0.001-0.4 M$  | Maahs (1983)                  |
| $v = k[O_3][S(IV)][H^+]^{-0.5}$                                   |   | pH 0-3<br>$T = 25^\circ C$                              | Martin (1984)                 |
| $v = k[O_3][HSO_3^-][H^+]^{-0.5}$                                 | $k = (1.45 \pm 0.7) \times 10^4 M^{-0.5} s^{-1}$  | pH 1-5<br>$T = 25^\circ C$                              | Penkett <i>et al.</i> (1979)  |
| $v = kP_{O_3}H_{O_3}[HSO_3^-][H^+]^{-0.1}$                        | $k = 4.4 \times 10^4 M^{-0.9} s^{-1}$   | pH 4-7<br>$T = 25^\circ C$                              | Larson <i>et al.</i> (1978)   |
| $v = k[Fe^{3+}][S(IV)][O_3][H^+]^*$                               | $k_{obs} = 6.8 \times 10^5 M^{-1} min^{-1} ppm^{-1}$  | pH 4-6<br>$T = 22^\circ C$<br>$[Fe^{3+}] \geq 10 \mu M$ | Harrison <i>et al.</i> (1982) |

$\text{HSO}_3^-$ , which then reacts with  $\text{O}_3$  via two separate pathways, one of which is base-catalyzed. As will be shown in subsequent paragraphs the empirical rate law of Maahs is virtually identical to those of Erickson *et al.* and Hoigne *et al.* when algebraically rearranged. The work of Penkett *et al.* and Martin clusters into another identifiable group in terms of the form of the empirical rate law and the magnitude of the observed rate constant. Reasons for this somewhat fortuitous agreement over a wide range of pH will be discussed in later portions of this paper. The work of Larson *et al.* and Harrison *et al.* shows less general agreement with the other investigators. Possible reasons for this disagreement have already been discussed by Maahs (1983b). There is clearly less agreement among the various investigators as to the mechanism(s) of the reaction. Penkett *et al.* favor a free radical mechanism that involves OH,  $\text{HSO}_3$ , and  $\text{HSO}_3$  as primary radicals; whereas Maahs (1983b) favors a polar pathway that proceeds via an electrophilic attack of  $\text{O}_3$  on the sulfur atom of  $\text{HOSO}_2^-$ ,  $\text{HSO}_3^-$ , or perhaps  $\text{SO}_3^{2-}$ . It should be pointed out that Maahs' proposed mechanism fails to account for the isotopic labelling experiments of Espenson and Taube (1965) that showed the incorporation of two labelled oxygen atoms into the product sulfate even though the stoichiometry [Equation (1)] requires the addition of only one oxygen atom to the reactant.

Future efforts in development of comprehensive atmospheric chemistry models, that incorporate aqueous-phase reactions, will require a self-consistent set of rate expressions, rate constants, and activation parameters applicable over a broad range of conditions (i.e. pH, concentration, and temperature). The goals of this paper are to analyze the composite set of data and observations reported by the above investigators in terms of a self-consistent rate expression, and to propose a mechanism(s) that is consistent with the generalized rate expression and with the ancillary mechanistic information such as the reported isotopic results and ionic strength dependence.

## RESULTS AND DISCUSSION

The raw kinetic data of Erickson *et al.* (1977), Hoigne *et al.* (1985), Maahs (1983b), Martin (1984) and Penkett *et al.* (1979) were analyzed in terms of the three-term rate law favored by Erickson *et al.* and Hoigne *et al.* Results of that analysis are presented in Table 2. The observed kinetic data of Maahs, Penkett *et al.* and Martin can be reinterpreted in terms of a multi-term rate law of the following form:

$$-d[\text{S(IV)}]/dt = (k_0\alpha_0 + k_1\alpha_1 + k_2\alpha_2)[\text{S(IV)}][\text{O}_3] \quad (2)$$

where

$$\alpha_0 = [\text{H}^+]^2/([\text{H}^+]^2 + k_{a1}[\text{H}^+] + K_{a1}K_{a2}) \quad (3)$$

$$\alpha_1 = K_{a1}[\text{H}^+]/([\text{H}^+]^2 + k_{a1}[\text{H}^+] + K_{a1}K_{a2}) \quad (4)$$

$$\alpha_2 = K_{a1}K_{a2}/([\text{H}^+]^2 + k_{a1}[\text{H}^+] + K_{a1}K_{a2}) \quad (5)$$

$$\alpha_0 + \alpha_1 + \alpha_2 = 1 \quad (6)$$

$$[\text{S(IV)}] = [\text{H}_2\text{O} \cdot \text{SO}_2] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}] \quad (7)$$

$$[\text{H}_2\text{O} \cdot \text{SO}_2] = \alpha_0[\text{S(IV)}] \quad (8)$$

$$[\text{HSO}_3^-] = \alpha_1[\text{S(IV)}] \quad (9)$$

$$[\text{SO}_3^{2-}] = \alpha_2[\text{S(IV)}] \quad (10)$$

The above rate law is algebraically equivalent in form to those used by Erickson *et al.* and Hoigne *et al.* with a few notational differences. The constants,  $k_0$ ,  $k_1$  and  $k_2$  show reasonable agreement for all five groups. The constants of Erickson *et al.*, Hoigne *et al.* and Maahs show the closest agreement which appears to reflect carefully controlled experiments. The range (pH 0–3) of experimental conditions used by Martin (1984) precluded the determination of  $k_2$  from his data; while the experimental conditions used by Penkett *et al.* (1979) (i.e. no pH control during a kinetic run) limited his data to the values of  $k_0$  and  $k_1$ . In the experiments of Penkett *et al.* at higher pH, the pH was not held constant during the course of a stopped-flow kinetic run. Given the magnitude of  $k_2$  the third term of the

Table 2. Intrinsic rate law for the oxidation of S(IV) by ozone

| Based on data from Erickson <i>et al.</i> (1977), Hoigne <i>et al.</i> (1984),<br>Maahs (1983), Martin (1984) and Penkett <i>et al.</i> (1979).   |                        |                             |                   |                   |                   |
|---|------------------------|-----------------------------|-------------------|-------------------|-------------------|
| $v = -d[\text{S(IV)}]/dt = (k_0\alpha_0 + k_1\alpha_1 + k_2\alpha_2)[\text{S(IV)}][\text{O}_3]$ $\alpha_0 = [\text{H}^+]^2/([\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2})$ $\alpha_1 = K_{a1}[\text{H}^+]/([\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2})$ $\alpha_2 = K_{a1}K_{a2}/([\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2})$ $\alpha_0 + \alpha_1 + \alpha_2 = 1$ $[\text{SO}_2 \cdot \text{H}_2\text{O}] = \alpha_0[\text{S(IV)}]$ $[\text{HSO}_3^-] = \alpha_1[\text{S(IV)}]$ $[\text{SO}_3^{2-}] = \alpha_2[\text{S(IV)}]$ $[\text{S(IV)}] = [\text{H}_2\text{O} \cdot \text{SO}_2] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}]$ |                        |                             |                   |                   |                   |
|   | Erickson               | Hoigne                      | Maahs             | Penkett           | Martin            |
| $k_0(\text{M}^{-1} \text{s}^{-1})$  | $\sim 5.9 \times 10^2$ | $(2.0 \pm 2.0) \times 10^4$ | —                 | $1.6 \times 10^4$ | $3.7 \times 10^4$ |
| $k_1(\text{M}^{-1} \text{s}^{-1})$  | $3.1 \times 10^5$      | $(3.2 \pm 0.2) \times 10^5$ | $3.9 \times 10^5$ | $4.5 \times 10^5$ | $1.2 \times 10^6$ |
| $k_2(\text{M}^{-1} \text{s}^{-1})$  | $2.2 \times 10^9$      | $(1.0 \pm 0.2) \times 10^9$ | $1.2 \times 10^9$ | —                 | —                 |
| $E_{a,1}(\text{kJ mol}^{-1})$   | 46.0                   | —                           | 33.9              | 30.0              | —                 |
| $E_{a,2}(\text{kJ mol}^{-1})$   | 43.9                   | —                           | 30.7              | —                 | —                 |

rate law can be shown to dominate the overall observed rate between pH 4 and 5. With the extremely rapid production of  $H^+$  in this pH domain, the pH of the reacting solution dropped to below pH 4. In this pH range, Penkett *et al.*'s observed kinetic results reflected primarily the  $k_1$  term. Therefore when they assumed that they were following the reaction at pH 5 they were in fact observing changes at much lower pH. The data generated by Maahs (1983b) at higher pH is reliable because he employed buffers to maintain a constant pH. The data of Erickson *et al.* were obtained in a pH domain in which the *in situ* production of acidity had a negligible impact on the pH of the reacting solution. Martin's data were collected over a similar pH range, although his data yield an intrinsic value of  $k_1$  which is approximately a factor of three higher than the other four research groups. There is no obvious explanation for this discrepancy. Dasgupta (1980) has pointed out previously the apparent agreement between the calculated  $k_1$  values for Penkett *et al.* and Erickson *et al.* In his comparison, he assumed that the three-term rate law of Erickson *et al.* was of the correct form.

In general the kinetic data of Erickson *et al.*, Maahs and Hoigne *et al.* appear to be the most self-consistent and reliable for application over a broad range of pH. A detailed analysis of the generalized rate law of Equation (2) for all of the above investigators is presented in Figs 1 and 3. Both open-phase (i.e. gas transfer is allowed to take place across a gas-water interface) and closed-phase (i.e. homogeneous aqueous phase reactions only) systems involving S(IV),  $O_3$ , and  $H^+$  are considered. Values for  $K_{a1}$ ,  $K_{a2}$ ,  $H_{SO_2}$ , and  $H_{O_3}$  have been taken from Jacob and Hoffmann (1983); the liquid water content (LWC) of the cloud water droplets ( $D_p = 10 \mu m$ ) was assumed to be  $0.2 g m^{-3}$  at  $25^\circ C$ ; the overall rate of reaction was assumed to be free of mass transfer limitations, even though this

assumption may be somewhat tenuous at higher pH (Martin, 1983). Reaction rates per investigator were calculated for the pH ranges of 0–7 and –1–7. Results were shown in Figs 1 and 2 for an open-phase system with gas phase concentrations of  $P_{SO_2} = 20$  ppb and  $P_{O_3} = 50$  ppb for each investigator using the unified rate law of Equation (2) and the constants and parameters given in Tables 2 and 3. Fairly close agreement is shown for all the groups over the pH range 1–4. In this pH domain the  $k_1$  term is dominant. The slightly higher value for  $k_1$  from Martin's data shows up clearly in these comparisons. Over the pH range of 4–7 there is much greater discrepancy among the investigators represented in this analysis. This is due to the fact that the  $k_2$  term begins to dominate above pH 4. Since  $k_2$  values could not be extracted from the Martin and Penkett *et al.* data sets, they were not factored into the overall rate expression. Erickson *et al.*, Maahs and Hoigne *et al.* show overall conversion rates that are a factor of 100 higher than the rates predicted by Martin and Penkett *et al.* at pH 6. At pH 5 given the above conditions the former groups predict an overall conversion rate with respect to the gas phase  $[SO_2]$  of  $10\% h^{-1}$ , while the latter groups predict a rate of only  $1\% h^{-1}$ .

The pH dependency of the overall reaction rate can be seen more clearly in Figs 3 and 4 for a closed- and open-phase reaction system, respectively. Kinetic constants from the Hoigne *et al.* data set have been used to construct these plots. The complex pH dependency for the closed-system reaction is shown in Fig. 5. Since all of the above investigators studied the kinetics of the S(IV)-ozone reaction in closed systems, this figure is most appropriate for explaining the variable  $[H^+]$  dependence that is reported in Table 1. Over the pH range of 5–7 the slope of the log rate vs pH plot is close to 1 (i.e.  $-0.89$  in terms of  $\log [H^+]$ ), while over the pH range of 0–2 the slope is close to 0.5 (i.e.  $-0.45$  in terms of  $\log [H^+]$ ). In the transition regime between pH 2 and 4, the slope is 0.34 (i.e.  $-0.34$  in terms of  $\log$

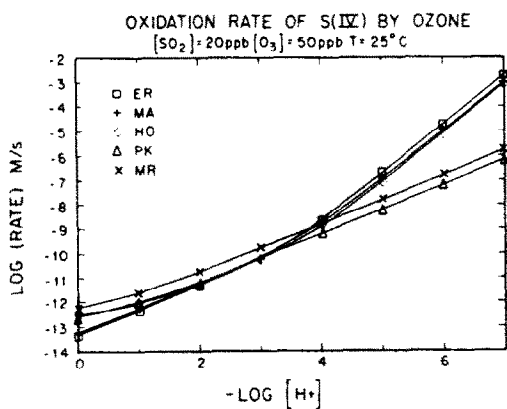


Fig. 1. A comparison plot of the rate of S(IV) oxidation by ozone as a function of pH predicted by the empirical rate laws of Table 1 for gas-phase concentrations typical of Los Angeles. Rate laws of Erickson *et al.*, Maahs, Hoigne *et al.*, Penkett *et al.* and Martin have been compared. Reaction rate is shown in units of moles  $l^{-1} s^{-1}$  based on the liquid phase.

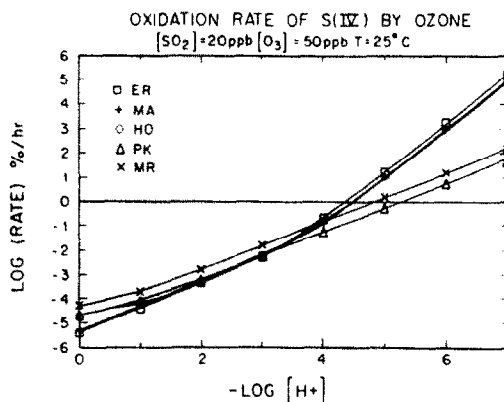


Fig. 2. A comparison plot of the rate of S(IV) oxidation by ozone as a function of pH. Same conditions as for Fig. 1. Reaction rates in this case are shown in units of  $\% h^{-1}$  based on the total conversion of S(IV) within a cubic meter of air.

Table 3. Kinetic data analysis for the S(IV)-ozone reaction

|   |                        |          |          |          |          |
|---|------------------------|----------|----------|----------|----------|
| Input data: equilibrium constants, pH, partial pressures, temperature |                        |          |          |          |          |
| $H(SO_2) = 1.24 \text{ (M atm}^{-1}\text{)}$                          | $pK_1 = 1.89$          |          |          |          |          |
| $H(O_3) = 0.01 \text{ (M atm}^{-1}\text{)}$                           | $pK_2 = 7.22$          |          |          |          |          |
| $P(SO_2) = 2.00 \times 10^{-8} \text{ (atm)}$                         | $T(^{\circ}C) = 25.00$ |          |          |          |          |
| $P(O_3) = 5.00 \times 10^{-8} \text{ (atm)}$                          | $pH = -1.0-7.0$        |          |          |          |          |
| Rate law, concentrations and ionization fractions                     |                        |          |          |          |          |
| $R = (k_0\alpha_0 + k_1\alpha_1 + k_2\alpha_2)[S(IV)][O_3]$           |                        |          |          |          |          |
| $[S(IV)] = H(SO_2)P(SO_2)/\alpha_0$                                   |                        |          |          |          |          |
| $[O_3] = H(O_3)P(O_3)$  |                        |          |          |          |          |
| Rate constants, activation energies, reaction rates per investigator  |                        |          |          |          |          |
|   | Erickson               | Maahs    | Hoigne   | Penkett  | Martin   |
| $k_0 \text{ (M}^{-1} \text{s}^{-1}\text{)}$                           | *****                  | *****    | 2.00E+04 | 1.60E+04 | 3.70E+04 |
| $k_1 \text{ (M}^{-1} \text{s}^{-1}\text{)}$                           | 3.10E+05               | 3.90E+05 | 3.20E+05 | 4.50E+05 | 1.20E+06 |
| $k_2 \text{ (M}^{-1} \text{s}^{-1}\text{)}$                           | 2.20E+09               | 1.20E+09 | 1.00E+09 | *****    | *****    |
| Temp. ( $^{\circ}C$ )   | 25.00                  | 25.00    | 22.00    | 25.00    | 25.00    |
| $E_a, k_1 \text{ (kJ mol}^{-1}\text{)}$                               | 46.00                  | 33.90    | *****    | *****    | *****    |
| $E_a, k_2 \text{ (kJ mol}^{-1}\text{)}$                               | 43.90                  | 30.70    | *****    | *****    | *****    |
| Rate (M s $^{-1}$ ) pH 5  | 2.02E-07               | 1.14E-07 | 9.46E-08 | 6.71E-09 | 1.79E-08 |
| Rate (M h $^{-1}$ ) pH 5  | 7.28E-04               | 4.09E-04 | 3.40E-04 | 2.41E-05 | 6.44E-05 |
| LWC (g m $^{-3}$ )  | 0.20                   | 0.20     | 0.20     | 0.20     | 0.20     |
| Rate (mol m $^{-3}$ h $^{-1}$ )                                       | 1.46E-07               | 8.18E-08 | 6.81E-08 | 4.83E-09 | 1.29E-08 |
| $P(SO_2)/RT \text{ (mol m}^{-3}\text{)}$                              | 8.18E-07               | 8.18E-07 | 8.18E-07 | 8.18E-07 | 8.18E-07 |
| Rate (% h $^{-1}$ ) pH 5  | 1.78E+01               | 1.00E+01 | 8.32E+00 | 5.90E-01 | 1.57E+00 |

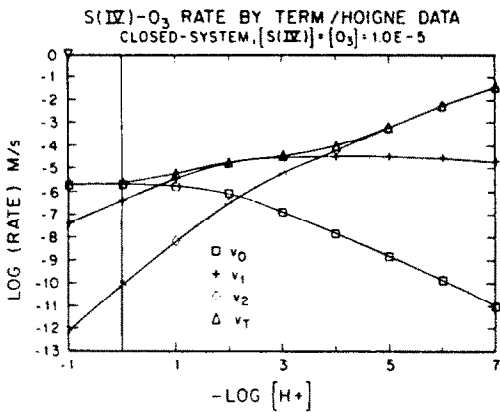


Fig. 3. A plot of reaction rate vs pH for the various terms of the multi-term rate law of Hoigne *et al.* (1984). The total rate of conversion as given by the summation of all three terms in the rate law is indicated by  $v_T$ . The calculations have been made for a closed-system (i.e. no gas-phase interaction considered).

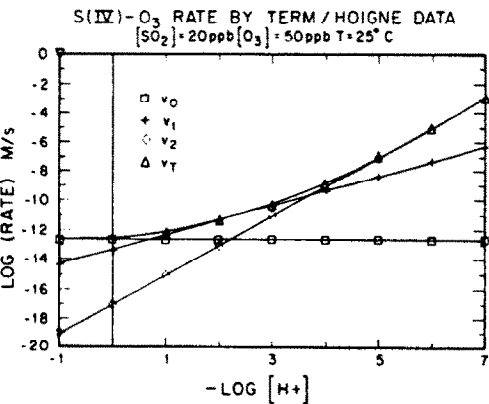


Fig. 4. Same considerations as for Fig. 3 except that an open-phase system was treated given conditions typical of the Los Angeles atmosphere

[H<sup>+</sup>]); and finally in the extreme low pH end of the scale no pH dependency is predicted. Therefore, depending on the pH range studied by the above groups, a different pH dependency may be ascertained especially over a limited pH range. Only the data of Hoigne *et al.* cover a sufficiently broad pH range to verify the exact pH dependency. This dependency arises because of the various alpha terms used in the overall rate equation. From a perusal of Equations (2-5) under various limiting conditions, the apparent [H<sup>+</sup>] dependencies can be readily seen. From pH 5 to 7, the third term in Equation (2) begins to dominate. In Equation (5) the dominant term in the denominator is the  $K_{a1}[H^+]$  term. This limiting case clearly gives a reciprocal first-order dependence on [H<sup>+</sup>]. Over the pH range of 2-4, the term involving  $\alpha_1$  is dominant. The limiting condition for this case can be deduced

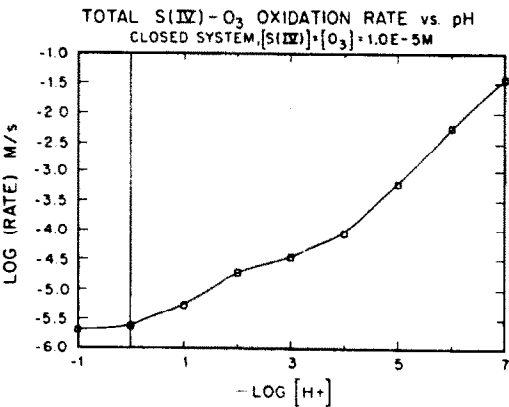


Fig. 5. The total S(IV)-O<sub>3</sub> oxidation rate vs pH using the rate law given by Hoigne *et al.* for a closed system. This plot helps to explain the different pH-dependencies reported by various investigators, that were in turn functions of the pH domains they chose to study.

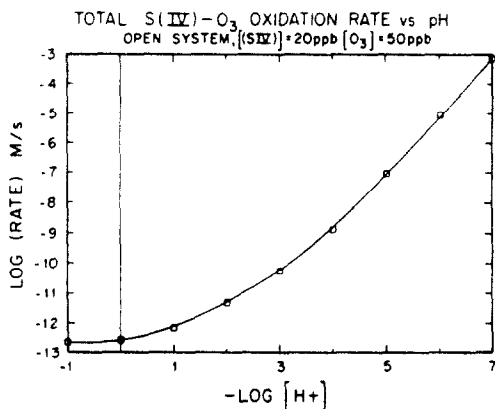


Fig. 6. The same comparison as described in the caption of Fig. 5 except that the system under consideration is now an open-phase system with conditions typical of the Los Angeles atmosphere.

from Equation (4), which shows that two terms in the denominator are of comparable magnitude (i.e.  $[H^+]^2$  and  $K_{a1}[H^+]$ ). This will have the net effect of producing a variable, fractional and reciprocal dependence on  $[H^+]$ .

The contribution of each individual term in the overall rate equation is illustrated for both the open and closed-phase systems in Figs 5 and 6. As described above, the  $k_2$  term is the dominant contributor to the overall rate above pH 4. Consequently, if this term is ignored as in the case of data of Martin (1984) and

Penkett *et al.* (1979), then the actual transformation rate will be under-predicted.

Since the rate law of Equation (2) has three separate terms, there must be three individual transition states of the elemental composition given in each term, respectively (Edwards *et al.*, 1968); and consequently, there must also be three separate mechanisms. Mechanisms consistent with the rate expression of Equation (2) and with the isotopic labelling results of Espenson and Taube (1965) are given in Figs 7, 8 and 9 for the kinetic terms involving  $H_2O \cdot SO_2$ ,  $HSO_3^-$  and  $SO_3^{2-}$ , respectively. The mechanisms presented in Figs 7-9 can be described as polar reactions (i.e. non-radical) that proceed via an electrophilic attack of  $O_3$  on the S(IV) center of each species. The starred oxygens indicate 0-18 labelling. After electron transfer, either a pentacoordinate or hexacoordinate intermediate is formed. These ozonide intermediates rearrange to give doubly-labelled sulfate and singly-labelled oxygen. These mechanisms offer a straightforward explanation for the isotopic labelling results of Espenson and Taube (1965), who have clearly shown that two 0-18 from the labelled  $O_3$  are incorporated in the product sulfate. Alternatively, the general mechanism could be described as a nucleophilic attack by S(IV) on  $O_3$ . This latter explanation is perhaps a more appropriate description in that the nucleophilic reactivity of S(IV) will increase in the order of  $H_2O \cdot SO_2 < HSO_3^- < SO_3^{2-}$  (Hoffmann, 1977; Hoffmann and Edwards, 1977; Edwards, 1965). The nucleophilic reactivity on the Edwards' scale is a function of the species basicity and electrode potential (Edwards, 1965).

$$\log(k/k_0) = \alpha \cdot E_n + \beta \cdot H \quad (11)$$

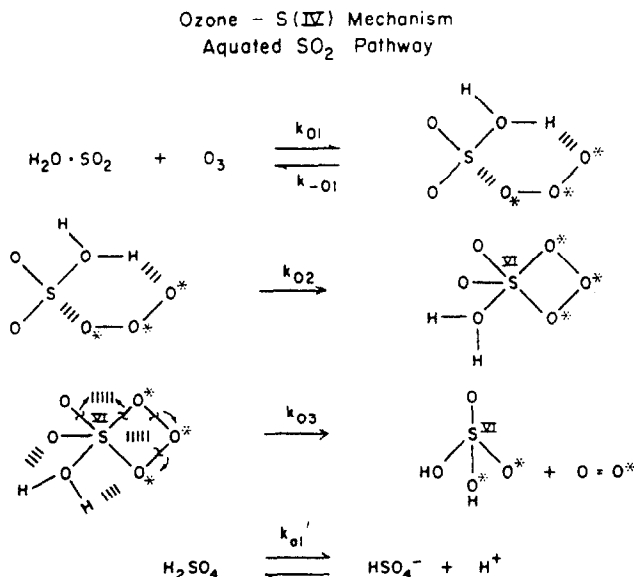


Fig. 7. A mechanism postulated for the first-term of the intrinsic rate expression of Table 2. In this case, the reaction proceeds via a nucleophilic attack on ozone by aqueated sulfur dioxide. The \*s indicated 0-18 labelled ozone. This mechanism is consistent with the results of isotopic labelling experiments of Espenson and Taube (1965).

Ozone - S(IV) Mechanism  
Bisulfite Pathway

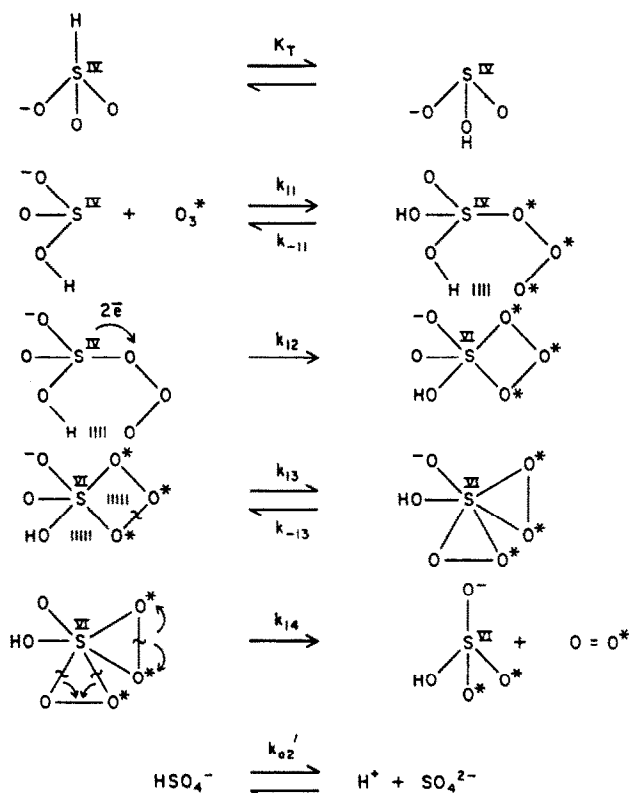


Fig. 8. A mechanism postulated for the second-term of the multi-term rate law for the oxidation of S(IV) by ozone. In this case, the reaction proceeds via a nucleophilic attack on ozone by bisulfite. The \*s indicated O-18 labelled ozone. This mechanism is also consistent with the results of isotopic labelling experiments.

where

$$E_n = E^0 + 2.6 \quad (12)$$

$$H = pK_a + 1.74 \quad (13)$$

and  $\alpha$  and  $\beta$  are the substrate constants.  $E_n$ , which is a nucleophilic constant characteristic of the particular electron donor, depends on the polarizability.  $E_n$  for  $\text{SO}_3^{2-}$  is 2.57 and for  $\text{HSO}_3^-$  2.13; while  $H$  is 8.96 and 3.69, respectively. In this case  $H$ , which reflects the relative basicity of the nucleophile, dominates the apparent reactivity. The observed ratio of  $k_2$  to  $k_1$  can be rationalized in terms of the relative sums of  $E_n$  and  $H$  assuming that  $\alpha$  and  $\beta$  are each close to 1. Therefore it can be predicted that  $\text{SO}_3^{2-}$  should react more rapidly with  $\text{O}_3$  than  $\text{HSO}_3^-$  and bisulfite should react more rapidly in turn than  $\text{H}_2\text{O} \cdot \text{SO}_2$ . A similar relative scale of nucleophilic reactivity has been shown by Hoffmann and Edwards (1977) and Leung and Hoffmann (1985) for nucleophilic displacements on  $\text{H}_2\text{O}_2$ , although the reaction of S(IV) with  $\text{H}_2\text{O}_2$  is an exception. This exception will be invoked later to argue for  $\text{HOSO}_2^-$  as the principal reactive bisulfite species.

The rate expressions that are derived from the mechanisms shown in Figs 7-9 are given below. They

were obtained by assuming that the  $k_{02}$ ,  $k_{12}$ , and  $k_{22}$  are the rate-limiting steps in each mechanism and that the steady-state approximation can be applied around each precursor intermediate.

$$v_0 = (k_{02}k_{01}/\{k_{-01} + k_{02}\})[\text{H}_2\text{O} \cdot \text{SO}_2][\text{O}_3] \quad (14)$$

$$v_1 = (k_{12}k_{11}/\{k_{-11} + k_{12}\})[\text{HSO}_3^-][\text{O}_3] \quad (15)$$

$$v_2 = (k_{22}k_{21}/\{k_{-21} + k_{22}\})[\text{SO}_3^{2-}][\text{O}_3] \quad (16)$$

where

$$k_0 = k_{02}k_{01}/\{k_{-01} + k_{02}\} \quad (17)$$

$$k_1 = k_{12}k_{11}/\{k_{-11} + k_{12}\} \quad (18)$$

$$k_2 = k_{22}k_{21}/\{k_{-21} + k_{22}\} \quad (19)$$

and

$$v_T = v_0 + v_1 + v_2 \quad (20)$$

which is algebraically equivalent to Equation (2).

Maahs (1983b) has proposed a somewhat similar mechanism to that given in Fig. 8, although he has assumed that the sulfur-hydrogen bonded bisulfite is the principle reactive form of S(IV). He then uses an

Ozone - S(IV) Mechanism  
Sulfite Pathway

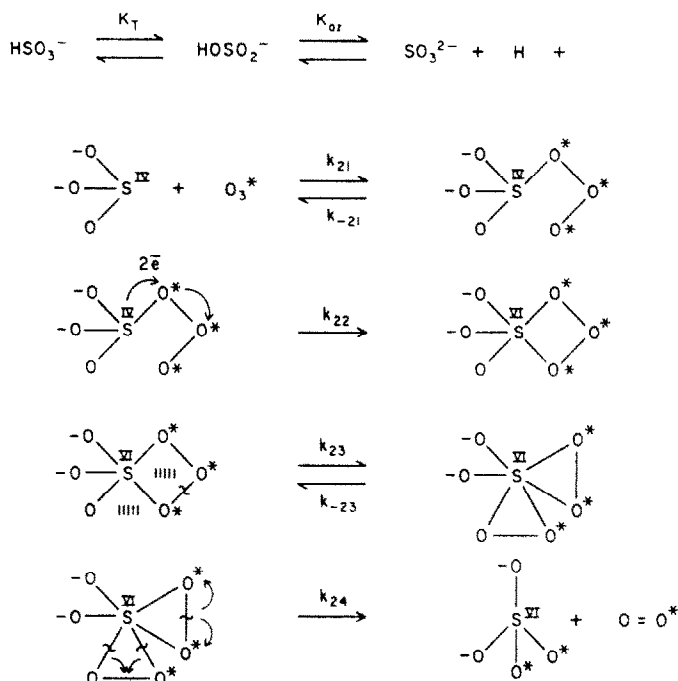


Fig. 9. A mechanism postulated for the third-term of the multi-term rate law for the oxidation of S(IV) by ozone. The reaction proceeds via the nucleophilic attack on ozone by sulfite. The \*s indicated O-18 labelled ozone. This mechanism is consistent with the results of isotopic labelling experiments.

observed positive ionic strength dependence with a slope of +1 to conclude that two monovalent, negatively charged species are reacting in the rate-limiting step of the mechanism. Therefore, he has proposed that  $\text{OH}^-$  and  $\text{HSO}_3^-$  react in a rate-limiting step. However, Moore and Pearson (1981) and Bunnet (1974) recommend that caution be used in the liberal application of ionic-strength dependencies for deducing a mechanism. Given the variable ionic-strength dependence as a function of pH as observed by Maahs (Maahs' Fig. 4), a more likely explanation for the observed dependence is a secondary ionic-strength effect in which the values of  $K_{a1}$  and  $K_{a2}$  are being shifted dramatically downward as the ionic strength is increased. For example at  $\mu = 0$ ,  $pK_{a2} = 7.22$  while at  $\mu = 1.0$  the same constant is 6.34. The net effect of this upward shift in  $K_{a2}$  is to increase the relative fraction of  $\text{SO}_3^{2-}$  at the same pH and consequently to increase the apparent overall rate of reaction because of an increased contribution by the  $k_2$  term. Therefore, at pH 5 Maahs should in fact have seen a slope of approximately one in his Davies' equation plot (Maahs' Fig. 4). However, as he shifted the pH downward to 3.0, the relative contribution of the  $k_2$  term diminishes and the apparent rate is then controlled by the  $k_1$  term which is more critically dependent on the value of  $K_{a1}$ . The value of  $K_{a1}$  varies from 1.89 at  $\mu = 0$  to 1.37 at  $\mu$

$= 1.0$ . At pH 3 the apparent increase in rate with an increase in ionic strength is due to the combined effect of upward shifts in both  $K_{a1}$  and  $K_{a2}$ , however, a Davies' plot slope of less than one would be expected. Maahs reports a slope of 0.7 at pH 3.1. I would interpret this preferentially in terms of a secondary ionic-strength effect rather than a primary effect as concluded by Maahs.

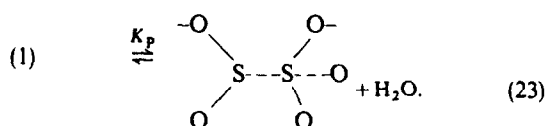
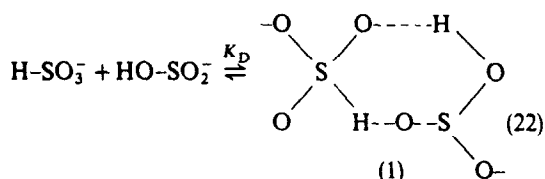
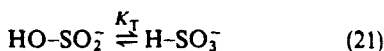
Furthermore, I have to question Maahs' assertion that the  $\text{H-SO}_3^-$  form of bisulfite is the predominant tautomer as opposed to the  $\text{HO-SO}_2^-$  form. He cites the work of Guthrie (1979) in support of his contention that  $\text{H-SO}_3^-$  is predominant with  $[\text{H-SO}_3^-]/[\text{HO-SO}_2^-] = 40$ . Guthrie's conclusions were drawn on the basis of the Linear Free Energy Relationship (LFER) between dimethyl sulfite and aquated sulfur dioxide ( $\text{H}_2\text{O} \cdot \text{SO}_2$ ). Care must be exerted when constructing a LFER among species that do not constitute an obvious homologous series (Edwards, 1965). Many assumptions go into the construction of a LFER. One of the critical ones is that the entropy changes for a homologous series of compounds are constant. This assumption most likely will not hold for  $(\text{CH}_3\text{O})_2\text{SO}$  and  $\text{H}_2\text{O} \cdot \text{SO}_2$  which differ dramatically in terms of their polarity (i.e the entropy of solvation should not be the same for both). Cotton and Wilkinson (1981) claim that there is no conclusive



evidence for the existence of a tautomeric equilibrium, as shown in Equation (21).



Stromberg *et al.* (1983) have concluded that  $\text{HO-SO}_2^-$  is the more stable tautomer by  $16 \text{ kJ mol}^{-1}$  based on *ab initio* calculations. However, they are cautious to state that in aqueous solution both most likely will coexist in approximately equal proportions. Golding (1960) has argued that both species co-exist in solution but that  $\text{HO-SO}_2^-$  dominates the u.v. spectrum of  $\text{S(IV)}$  due to its single empty  $\pi$ -orbital and greater oscillator strength for the first electronic transition. He concluded that at low concentrations (i.e.  $[\text{S(IV)}] \leq 10^{-3} \text{ M}$ ), the  $\text{HO-SO}_2^-$  species predominates. At higher concentrations the two bisulfite tautomers form a dimer which eventually dehydrates to form pyrosulfite,  $\text{S}_2\text{O}_3^{2-}$ , as shown below



Recent Raman and u.v. measurements by Connick *et al.* (1982) substantiate Golding's arguments (1960) for the coexistence of both tautomers in aqueous solution. In addition, they determined that overall pyrosulfite formation constant,  $K_P (K_P = K_T K_D K_P)$ , is  $0.088 \text{ M}^{-1}$  as compared to Golding's value of  $0.07 \text{ M}^{-1}$  at ionic strength of  $0.1 \text{ M}$  and Bourne *et al.*'s (1974) value of  $0.115$  at the same ionic strength. Recently, Rhee and Dasgupta (1985) have determined an overall dimerization constant,  $K_D (K_D = K_T K_D)$ , of  $1.75 \times 10^3 \text{ M}^{-1}$  at  $25^\circ\text{C}$ . Theoretical work of Meyer *et al.* (1977) and Baird and Taylor (1981) suggests that the H-S bonded tautomer is the most energetically favorable. However, Stromberg *et al.* (1983) argue that the latter two papers lack computational rigor and therefore their conclusions are suspect.

The chemical reactivity of bisulfite can be best explained in terms of the  $\text{HO-SO}_2^-$  tautomer as the predominant species provided that the two tautomers are in rapid equilibrium. For example, the kinetics and mechanism of the  $\text{H}_2\text{O}_2$ -bisulfite reaction, which occurs via a nucleophilic attack by hydrogen peroxide on bisulfite, suggest that the pyramidal,  $\text{HO-SO}_2^-$ , form would provide a stereochemically more attractive site for attack by a nucleophile than the tetrahedral tautomer. The latter would clearly be more sterically hindered and consequently require a higher activation

free energy,  $\Delta G^\ddagger$ . Likewise, the electrophilic attack of  $\text{O}_3$  on the pyramidal  $\text{HO-S}$  form of bisulfite should be more facile than attack on the tetrahedral H-S bonded form.

## CONCLUSIONS

Kinetic data obtained from a number of different investigators on the reaction of  $\text{S(IV)}$  with  $\text{O}_3$  in aqueous solution have been analyzed in terms of a single self-consistent rate expression. The rate expression that most appropriately fits all kinetic observations treated in this study is:

$$-d[\text{S(IV)}]/dt = (k_0\alpha_0 + k_1\alpha_1 + k_2\alpha_2)[\text{S(IV)}][\text{O}_3].$$

This kinetic expression is similar in form to the empirical rate laws reported by Erickson *et al.* (1977) and Hoigne *et al.* (1985). The recommended values for  $k_0$ ,  $k_1$ , and  $k_2$  are  $(2.4 \pm 1.1) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ,  $(3.7 \pm 0.7) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , and  $(1.5 \pm 0.6) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. The activation energies that are recommended for  $k_1$  and  $k_2$  are taken from Erickson *et al.* (1977) as  $46.0 \text{ kJ mol}^{-1}$  and  $43.9 \text{ kJ mol}^{-1}$ , respectively. The reaction proceeds via three independent pathways that involve a nucleophilic attack on  $\text{O}_3$  by  $\text{SO}_3^{2-}$ ,  $\text{HO-SO}_2^-$ , and  $\text{SO}_2 \cdot \text{H}_2\text{O}$ . Arguments for the existence of  $\text{HO-SO}_2^-$  as the predominant form of bisulfite in aqueous solution are presented. Rate laws and kinetic data of five investigators are compared for an open cloud water system with a liquid water content of  $0.2 \text{ g m}^{-3}$ .

**Acknowledgements**—Special thanks are extended to Dr Jack G. Calvert of the National Center for Atmospheric Research for providing the support, space, time and encouragement to write this paper, and to Dr Marcia Dodge, U.S. EPA Project Officer, for providing financial support through Interagency Agreement DW 930237. This work was performed while the author was a Visiting Scientist at NCAR.

## REFERENCES

- Baird N. C. and Taylor K. F. (1981) *Ab initio* MO calculations for the oxides, oxyacids, and oxyanions of  $\text{S(IV)}$  and  $\text{S(VI)}$ . *J. Computational Chem.* **2**, 225–230.
- Bourne D. W., Higuchi T. and Pitman I. H. (1974) Chemical equilibria in solutions of bisulfite salts. *J. Pharm. Sci.* **63**, 865–868.
- Boyce S. D. and Hoffmann M. R. (1984) Kinetics and mechanism of the formation of hydroxymethanesulfonic acid at low pH. *J. phys. Chem.* **88**, 4740–4746.
- Boyce S. D., Hoffmann M. R., Hong P. A. and Moberly L. M. (1983) Catalysis of the autoxidation of aquated sulfur dioxide by homogeneous metal-phthalocyanine complexes. *Envir. Sci. Technol.* **17**, 602–611.
- Bunnet J. F. (1974) From kinetic data to reaction mechanism. In *Investigations of Rates and Mechanisms of Reactions Part I*, 3rd. edn (edited by Lewis E. S.). Wiley-Interscience, New York.
- Connick R. E., Tam T. M. and von Deuster E. (1982) Equilibrium constant for the dimerization of bisulfite ion to form pyrosulfite. *Inorg. Chem.* **21**, 103–107.
- Cotton F. A. and Wilkinson G. (1981) *Advanced Inorganic Chemistry*, p. 532. Wiley, New York.
- Dasgupta P. K. (1980) Discussion: the importance of atmos-

- pheric ozone and hydrogen peroxide in oxidizing sulfur dioxide in cloud and rainwater. *Atmospheric Environment* **14**, 272-275.
- Edwards J. O. (1965) *Inorganic Reaction Mechanisms*, pp. 51-71. Benjamin, New York.
- Edwards J. O., Greene E. F. and Ross J. (1968) From stoichiometry and rate law to mechanism. *J. Chem. Educ.* **45**, 381-385.
- Erickson R. E., Yates L. M., Clark R. L. and McEwen D. (1977) The reaction of sulfur dioxide with ozone in water and its possible atmospheric significance. *Atmospheric Environment* **11**, 813-817.
- Espenson J. H. and Taube H. (1965) Tracer experiments with ozone as oxidizing agent in aqueous solution. *Inorg. Chem.* **4**, 704-709.
- Golding R. M. (1960) Ultraviolet absorption studies of the bisulfite-pyrosulfite equilibrium. *J. Chem. Soc.* 3711-3716.
- Guthrie J. P. (1979) Tautomeric equilibria and  $pK_a$  values for sulfurous acid in aqueous solution: a thermodynamic analysis. *Can. J. Chem.* **57**, 454-457.
- Harrison H., Larson T. V. and Monkman, C. S. (1982) Aqueous phase oxidation of sulfites by ozone in the presence of iron and manganese. *Atmospheric Environment* **16**, 1039-1041.
- Hegg D. A. and Hobbs P. V. (1982) Measurement of sulfate production in natural clouds. *Atmospheric Environment* **16**, 2663-2668.
- Hoffmann M. R. (1977) Kinetics and mechanism of the oxidation of hydrogen sulfide by hydrogen peroxide in acidic solution. *Envir. Sci. Technol.* **11**, 61-66.
- Hoffmann M. R. and Boyce S. D. (1983) Catalytic autooxidation of aqueous sulfur dioxide in relationship to atmospheric systems. In *Trace Atmospheric Constituents: Properties, Transformations, and Sulfates* (edited by Schwartz S.). Wiley, New York. *Adv. Envir. Sci. Technol.* **12**, 147-189.
- Hoffmann M. R. and Edwards J. O. (1975) Kinetics and mechanism of the oxidation of sulfur dioxide by hydrogen peroxide in acidic solution. *J. phys. Chem.* **79**, 2096-2098.
- Hoffmann M. R. and Edwards J. O. (1977) Kinetics and mechanisms of the oxidation of thiourea and N,N-dialkylthioureas by hydrogen peroxide. *Inorg. Chem.* **16**, 3333-3338.
- Hoffmann M. R. and Jacob D. J. (1984) Kinetics and mechanisms of the catalytic oxidation of dissolved sulfur dioxide in aqueous solution: an application to night-time fog water chemistry. In *SO<sub>2</sub>·NO and NO<sub>2</sub> Oxidation Mechanisms: Atmospheric Considerations* (edited by Calvert J. G.), pp. 101-171. Butterworth, Boston.
- Hoigne J., Bader H., Haag W. R. and Staehelin J. (1985) Rate constants of reactions of ozone with organic and inorganic compounds in water—III. Inorganic compounds and radicals. *Water Res.* **19**, 993-1004.
- Jacob D. J. and Hoffmann M. R. (1983) A dynamic model for the production of H<sup>+</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in urban fog. *J. geophys. Res.* **88C**, 6611-6621.
- Leung P. K. and Hoffmann M. R. (1985) Kinetics and mechanism of the oxidation of 2-mercaptoethanol by hydrogen peroxide in aqueous solution. *J. phys. Chem.* **89**, 5267-5271.
- Maahs H. G. (1983a) Measurement of the oxidation rate of sulfur(IV) by ozone in aqueous solution and their relevance to sulfur dioxide conversion in nonurban tropospheric clouds. *Atmospheric Environment* **17**, 341-345.
- Maahs H. G. (1983b) Kinetics and mechanics of the oxidation of S(IV) by ozone in aqueous solution with particular reference to SO<sub>2</sub> conversion in nonurban tropospheric clouds. *J. geophys. Res.* **88C**, 10721-10732.
- Martin L. R. (1983) Measurement of sulfate production in natural clouds: a discussion. *Atmospheric Environment* **17**, 1603-1604.
- Martin L. R. (1984) Kinetic studies of sulfite oxidation in aqueous solution. In *SO<sub>2</sub>·NO and NO<sub>2</sub> Oxidation Mechanisms: Atmospheric Considerations* (edited by Calvert J. G.), pp. 63-100. Butterworth, Boston.
- McArdle J. V. and Hoffmann M. R. (1983) Kinetics and mechanism of the oxidation of aquated sulfur dioxide by hydrogen peroxide at low pH. *J. phys. Chem.* **87**, 5425-5429.
- Meyer B., Peter L. and Spitzer K. (1977) Trends in the charge distribution in sulfanes, sulfanesulfonic acids and sulfurous acid. *Inorg. Chem.* **16**, 27-33.
- Moore J. W. and Pearson R. G. (1981) *Kinetics and Mechanism*, 3rd. edn, pp. 272-275. Wiley, New York.
- Penkett S. A. (1972) Oxidation of SO<sub>2</sub> and other atmospheric gases by ozone in aqueous solution. *Nature* **240**, 105-106.
- Penkett S. A., Jones B. M., Brice K. A. and Eggleton A. E. (1979) The importance of atmospheric ozone and hydrogen peroxide in oxidizing sulfur dioxide in cloud and rainwater. *Atmospheric Environment* **13**, 123-137.
- Rhee J. S. and Dasgupta P. K. (1985) The second dissociation constant of SO<sub>2</sub>·H<sub>2</sub>O. *J. phys. Chem.* **89**, 1799-1804.
- Stromberg A., Gropen O., Wahlgren, U. and Lindqvist O. (1983) *Ab initio* calculations on the sulfite ion, SO<sub>3</sub><sup>2-</sup>, and hydrogen sulfite ion, HSO<sub>3</sub><sup>-</sup> or SO<sub>2</sub>OH<sup>-</sup>. *Inorg. Chem.* **22**, 1129-1133.