

Kinetics of oxidation of sulphur(IV) by peroxodisulphate: Relative reactivity of bisulphite and sulphite ions

Pinky Bhargava & K S Gupta*

Atmospheric Chemistry Laboratory, Department of Chemistry, University of Rajasthan, Jaipur 302 004

Received 12 March 1992; revised 13 August 1992; accepted 7 November 1992

In the pH region 4.3-8.5, the oxidation of sulphur(IV) by peroxodisulphate (Eq. i) obeys the experimental rate law (ii).



$$-\frac{d[\text{S(IV)}]}{dt} = \frac{k_{\text{SO}_3} K_{d(2)} + k_{\text{HSO}_3} [\text{H}^+]}{[\text{H}^+] + K_{d(2)}} [\text{PDS}][\text{S(IV)}] \quad \dots \text{(ii)}$$

where k_{SO_3} and k_{HSO_3} are bimolecular rate constants for the $\text{S}_2\text{O}_8^{2-} - \text{SO}_3^{2-}$ and $\text{S}_2\text{O}_8^{2-} - \text{HSO}_3^-$ reactions and $K_{d(2)}$ is the dissociation constant of $\text{HSO}_3^- \cdot k_{\text{SO}_3}$ and k_{HSO_3} values are 6×10^{-2} and $2.8 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ respectively at $I = 1.0 \text{ mol dm}^{-3}$ and 40°C .

Studies on the aqueous phase oxidation of dissolved sulphur dioxide, i.e. sulphur(IV) are important in understanding the atmospheric chemistry of this acid rain precursor¹. Its oxidation with dioxygen², hydrogen peroxide²⁻⁴, ozone⁵, organic peroxy-acids⁶ and peroxomonosulphate⁷ has been studied. It is noteworthy that while in the oxidation by oxygen² and ozone⁵ sulphite ion is much more reactive than bisulphite, the reverse is true with hydrogen peroxide²⁻⁴ and peroxomonosulphate⁷.

The interest in the present reaction emanated from a desire to compare the relative reactivity of sulphite and bisulphite ions in their oxidation with peroxodisulphate, peroxomonosulphate and other peroxy-oxidants. Previously, the kinetics of this reaction has been studied by Tan and House⁸ over pH 5 and the results were interpreted in terms of rate law (1). They assumed only sulphite ion to be reactive. In an

$$-\frac{d[\text{S(IV)}]}{dt} = \frac{kK[\text{S}_2\text{O}_8^{2-}][\text{S(IV)}]}{(K + [\text{H}^+])} \quad \dots \text{(1)}$$

earlier investigation, Fomina *et al.*⁹ determined kinetic orders in peroxodisulphate and sulphur(IV), but there is some confusion¹⁰ regarding the rate law.

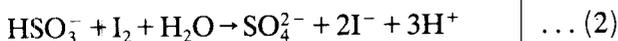
In the present investigation, the reaction has been studied over a wide pH range and the results

are in agreement with both sulphite and bisulphite ions being reactive.

Materials and Methods

Potassium peroxodisulphate (PDS) (E. Merck) and sodium sulphite (BDH) were used as such. All other chemicals were of reagent grade. As the autoxidation of S(IV) is trace-metal ion catalyzed, the kinetics were studied in the presence of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ EDTA to suppress this path and eliminate interference with the main PDS-S(IV) reaction¹¹. For study in the pH region 4.0-5.95 acetic acid-sodium acetate, and for higher pH studies potassium dihydrogen phosphate-disodium hydrogen phosphate buffers were used. For lower pH studies, perchloric acid was used for adjusting the initial pH. The ionic strength was maintained by use of sodium nitrate.

The kinetics were studied in closed reaction vessels which were immersed in a thermostated water bath ($\pm 0.1^\circ$). The kinetics were followed by withdrawing the aliquot samples and quenching the reaction with the use of ice cold water and cracked ice. Unreacted S(IV) was estimated by adding a known volume of standard iodine solution to the aliquots and back-titrating the unreacted iodine against standard sodium thiosulphate solution using starch as an indicator¹². The titration was performed in slightly acidic medium. The sulphur(IV)-iodine reaction (2) is so fast that



it is outside the time range of stopped-flow equipment¹³. Hence, even at low temperature, reaction (2) is essentially complete during the time required for mixing S(IV) and I₂ and hence the low temperature, at which estimation of S(IV) was done, did not affect the assay. The control experiments showed that the assay of sulphite, in the range of pH used in the present study, was unaffected by the presence and the absence of PDS. Obviously PDS-I⁻ and PDS-S₂O₃²⁻ reactions must be of no consequence. The rate of the thermal decomposition of PDS in the pH range 1.8-7.5 was found to be very slow as compared to the rate of its reduction by sulphur(IV) and hence there was no complication due to the former reaction. This is in agreement with the reported slowness of the decomposition under these conditions¹⁰.

Stoichiometry—The stoichiometric measurements were made by allowing equal amounts of PDS and S(IV) to react for sufficiently long time so as to ensure completion of the reaction. The qualitative analysis indicated sulphate to be present and dithionate to be absent. Quantitative estimation of sulphate in the final product solution was made by precipitating it as BaSO₄. The ratio of sulphate formed to that expected from Eq. (3) was found to be 0.96 ± 0.1, which is in accord with Eq. (3)



and also with the work of Fomina *et al.*⁹ and of Aten *et al.*¹⁴. The latter authors have reported that in acid medium PDS oxidized about 1% sulphur (IV) only into dithionate. However, our results are at variance with those of Tan and House⁸, who have indicated the formation of higher amounts of dithionate, using a different method for stoichiometric measurements.

Results

The rate measurements made with varying [S(IV)] (1.0-80.0 × 10⁻³ mol dm⁻³) and [PDS] (1.0-8.0 × 10⁻² mol dm⁻³) at pH = 5.02 and I = 1.0 mol dm⁻³ fitted the second order rate law (4).

$$-\frac{d[\text{S(IV)}]}{dt} = k_2[\text{PDS}][\text{S(IV)}] \quad \dots (4)$$

The value of second order rate constant, *k*₂, was found to be (8.3 ± 0.8) × 10⁻³ dm³mol⁻¹s⁻¹.

From some kinetic runs, carried out under pseudo-order conditions (with [PDS] in excess

over [S(IV)]), pseudo-first order rate constants, *k*₁, were obtained. The values of *k*₂ obtained from *k*₁ agreed with the values determined under second order conditions.

The effect of [H⁺] was studied by varying pH in the range 1.49-7.72. The results of pH range 4.30-7.72 are in agreement with the rate law (5).

$$k_2 = \frac{k_{\text{SO}_3} K_{\text{d}(2)} + k_{\text{HSO}_3} [\text{H}^+]}{[\text{H}^+] + K_{\text{d}(2)}} \quad \dots (5)$$

where *K*_{d(2)} is the dissociation constant of HSO₃⁻ and *k*_{SO₃} and *k*_{HSO₃} are the rate constants for the reactions of SO₃²⁻ and HSO₃⁻ with S₂O₈²⁻. Equation (5) can be rearranged as Eq. (6).

$$k_2([\text{H}^+] + K_{\text{d}(2)}) = k_{\text{SO}_3} K_{\text{d}(2)} + k_{\text{HSO}_3} [\text{H}^+] \quad \dots (6)$$

Using a recently determined value¹⁵ of 5.0 × 10⁻⁷ for *K*_{d(2)}, the plot of *k*₂([H⁺] + *K*_{d(2)}) versus [H⁺] was linear. The values of *k*_{SO₃} *K*_{d(2)} and *k*_{HSO₃} were found to be (3.0 ± 0.7) × 10⁻⁸ and (2.8 ± 0.40) × 10⁻³ dm³mol⁻¹s⁻¹ respectively at 40° and I = 1.0 mol dm⁻³ and from the former, a value of (6 ± 1) × 10⁻² dm³mol⁻¹s⁻¹ for *k*_{SO₃} was obtained.

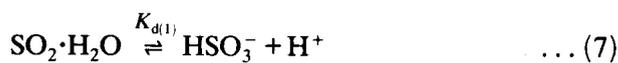
It is noteworthy that the rate is not affected by a decrease in pH below 4.30. Indeed, the value of *k*₂ is almost constant in the pH region 1.49-4.30 [(3.2 ± 0.4) × 10⁻³ dm³mol⁻¹s⁻¹]. It indicates that both SO₂.H₂O (which is predominant in low pH solutions) and HSO₃⁻ are almost equally reactive.

On increasing ionic strength from 0.1-1.0 mol dm⁻³ the rate almost doubled from 4.6 × 10⁻³ to 9.1 × 10⁻³ dm³mol⁻¹s⁻¹ at 40°C and pH 5.02. On increasing the concentration of mannitol, a free radical scavenger, *k*₂ decreased only marginally from a value of 11 × 10⁻³ dm³mol⁻¹s⁻¹ at 5 × 10⁻³ mol dm⁻³ mannitol to a value of 8.3 × 10⁻³ dm³mol⁻¹s⁻¹ at 15 × 10⁻³ mol dm⁻³ mannitol both at pH 5.82 and 40°C. Using Arrhenius equation, and the values of *k*₂ the energies of activation were determined to be 29 and 47 kJ mol⁻¹ at pH 5.02 and 8.5 respectively.

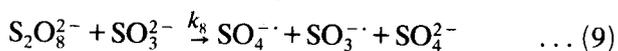
Discussion

The gross kinetics features are as follows. The reaction is first order in both PDS and sulphur (IV) which probably indicates involvement of both species in the slow step. The nature of hydrogen dependence requires both HSO₃⁻ and SO₃²⁻ to be reactive, as in the present pH conditions HSO₃⁻ and SO₃²⁻ only need be considered in consonance with reported values¹⁵ of *K*_{d(1)} (1.26 × 10⁻²) and

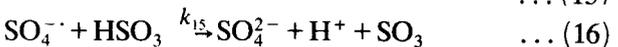
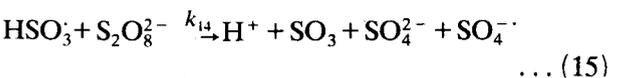
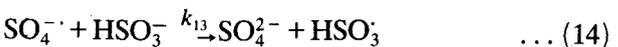
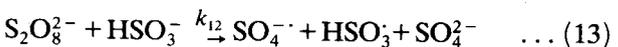
$K_{d(2)}$ (5.0×10^{-7}) for the acid dissociation equilibria (7,8).



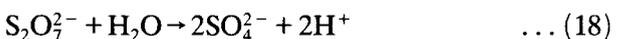
Recalling earlier work is helpful in proposing mechanism. The study of terminal groups of polymers obtained in the system containing peroxodisulphate and sulphite indicated the formation of $\text{SO}_4^{\cdot -}$ radical¹⁶. The comparative studies on PDS-S(IV) reaction, and on thermal decomposition of PDS in the presence of radical acceptors like *p*-nitrosodimethylaniline (NDMA), methanol and 2-propanol which compete for free radicals formed, showed the formation of $\text{SO}_4^{\cdot -}$ radicals in the primary step¹⁷. Based on this information and on the work of Wilmarth and Haim¹⁶, the following mechanism may be proposed.



and



A small rate decreasing effect of mannitol shows it to be a poor competitor for $\text{SO}_4^{\cdot -}$ radicals. The alternative non-radical mechanism (17,18)⁸ is ruled out on the basis of the work of



Lezina *et al.*¹⁷, as it will not explain the NDMA competition and polymerization experiments. The steps (8,9-16) will lead to rate law (19).

$$-\frac{d\text{S(IV)}}{dt} = \left[\left(\frac{k_8 k_9 k_{10}}{k_{11}} \right)^{1/2} K_{d(2)} + \left(\frac{k_{12} k_{13} k_{14}}{k_{15}} \right)^{1/2} [\text{H}^+] \right] \times \frac{[\text{S}_2\text{O}_8^{2-}][\text{S(IV)}]}{([\text{H}^+] + K_{d(2)})} \quad \dots (19)$$

which is same as experimental rate law (5) through

$$k_{\text{SO}_3} = \left(\frac{k_8 k_9 k_{10}}{k_{11}} \right)^{1/2} \quad \dots (20)$$

and

$$k_{\text{HSO}_3} = \left(\frac{k_{12} k_{13} k_{14}}{k_{15}} \right)^{1/2} \quad \dots (21)$$

A survey of rate constants¹⁹ shows k_{SO_3} for $\text{SO}_4^{\cdot -} - \text{SO}_3^{2-}$ to be more than $2.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and k_{HSO_3} for $\text{SO}_4^{\cdot -} - \text{HSO}_3^-$ reaction to be only 2.5 times this value. It can, therefore, be safely assumed that $k_9 \approx k_{13}$, $k_{10} \approx k_{14}$ and $k_{11} \approx k_{15}$ and then Eqs (20) and (21) lead to Eq. (22).

$$\frac{k_{\text{SO}_3}}{k_{\text{HSO}_3}} = \left(\frac{k_8}{k_{12}} \right)^{1/2} \quad \dots (22)$$

On substituting the values of k_{SO_3} and k_{HSO_3} obtained in this study in Eq. (22), one obtains $k_8/k_{12} \approx 10^3$. Interestingly, a similar reactivity ratio for SO_3^{2-} and HSO_3^- has been found with O_3 (Table 1) also. The ratio of rates of substitution²⁰ of SO_3^{2-} and HSO_3^- in the complexes *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{SO}_3)(\text{H}_2\text{O})]^2+$ and *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{HSO}_3)(\text{H}_2\text{O})]^+$ by pyrazine too has a similar value of $\sim 1 \times 10^3$. On the other hand, in the oxidation of S(IV) by H_2O_2 , peroxomonosulphate, methyl hydroperoxide and peroxyacetic acid, the reactivity trend is inverted, i.e., $k_{\text{HSO}_3} > k_{\text{SO}_3}$ (Table 1). On the basis of the relative k_{HSO_3} and k_{SO_3} values, the S(IV) oxidation reactions (Table 1) fall in two categories which occur by two different mechanisms. Hoffmann⁵ has explained the reactivity trend, $k_{\text{SO}_3} > k_{\text{HSO}_3}$, by postulating that the reactions involve a nucleophilic attack by SO_3^{2-} and HSO_3^- on O_3 , which is in accord with nucleophilicity order $\text{SO}_3^{2-} > \text{HSO}_3^-$. It is interesting to point out that in forming benzaldehyde-sulphur (IV) adducts²¹, the nucleophilicity of SO_3^{2-} and HSO_3^- is the main rate determining factor and almost a similar value of $\sim 10^4$ for $k_{\text{HSO}_3}/k_{\text{SO}_3}$ has been found. The reactivity order, $k_{\text{HSO}_3} > k_{\text{SO}_3}$, for peroxomonosulphate, and H_2O_2 and its derivatives has been explained by proposing a nucleophilic substitution mechanism which involves substitution of a $-\text{O}_2\text{X}$ group on sulphite sulphur. The presence of two $-\text{SO}_3$ groups on both sides of $-\text{O}-\text{O}-$ bond in PDS precludes the operation of this mechanism.

Table 1—Rate constant, k_{HSO_3} and k_{SO_3} , for the reaction of HSO_3^- and SO_3^{2-} with different oxidants

Oxidant	k_{SO_3} $\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$	k_{HSO_3} $\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$	Reference
Potassium peroxodisulphate	6.0×10^{-2}	2.8×10^{-3} (40° , $I=1.0 \text{ mol dm}^{-3}$) 8.20×10^{-3} (25°C , $I=1.0 \text{ mol dm}^{-3}$)	This work (8)
Peroxomonosulphate	—	1.21×10^6 (5° , $I=0.2 \text{ mol dm}^{-3}$)	(7)
Ozone	1.5×10^9	3.70×10^5 (25°)	(3)
Hydrogen peroxide	—	7.2×10^7 (18°)	(6)
	0.20 (25°)	—	(4)
		3.5×10^8 (12°)	(3)
Methylhydroperoxide	—	1.7×10^7 (23°)	(6)
Peroxyacetic acid	—	3.5×10^7 (18°)	(6)

The rate constants for PDS reaction (Table 1) are several orders of magnitude lower than for others and this could possibly be due to steric hindrance caused by the presence of two $-\text{SO}_3$ groups on both sides of $-\text{O}-\text{O}-$ linkage. A preliminary investigation in this laboratory revealed the reaction between peroxodiphosphate and S(IV), under similar conditions, to be almost imperceptible.

The energy of activation in the present case is similar in magnitude to that in the oxidation of I^- , Fe^{2+} and several Fe(II) and Os(II) complexes, but much lower than the energy of $\sim 141 \text{ kJ mol}^{-1}$ for homolysis of peroxide bond¹⁸. The much lower energy of activation for these reactions¹ has been taken as being indicative of the stabilization of activated complexes caused by transfer of an electron from the S(IV) to a nascent sulphate radical ion as in Eq. (23) which supports the steps (9) and (13) in the mechanism proposed by us.



Acknowledgement

The work was supported by an Indo-US Project CE-2. The authors are grateful to Dr. R.E. Huie, NIST, Gaithersburg, MD, USA for suggestions on the free radical aspects of this reaction.

References

- SO_2 , NO_2 and NO oxidation mechanisms. *Atmospheric considerations*, edited by J G Calvert (Butterworth, Boston) 1984.
- Martin L R, SO_2 , NO and NO_2 oxidation mechanisms. *Atmospheric considerations*, edited by J G Calvert (Butterworth, Boston) 1984, pp 67-68.
- Hoffmann M R & Edwards J O, *J phys Chem*, 79 (1975) 2096-2098.
- Mader P M, *J Am chem Soc*, 80 (1958) 2634.
- Hoffmann M R, *Atmos Environ*, 20 (1986) 1145.
- Lind Z A, Lazrus A L & Kok G L, *J Geophys Res*, 92 (1987) 4171.
- Betterton E A & Hoffmann M R, *J phys Chem*, 92 (1982) 5962.
- Tan L C & House D A, *New Zealand J Sci*, 17 (1974) 319.
- Formina T V, Dymarchuk N P & Mishchenko K P, *Zh Prikl Khim*, 41 (1968) 982 & 2440.
- Wilson I R, *Comprehensive chemical kinetics*, 6 (1972) 340-350.
- Huss Jr A, Lim P K & Eckert C A, *J Am chem Soc*, 100 (1978) 6252-6253.
- Rani A, Prasad D S N, Bhargava R & Gupta K S, *Bull chem Soc Japan*, 64 (1991); Rani A, Prasad D S N, Madanawat P V S & Gupta K S, *Atmos Environ*, 26A (1992) 67.
- Rani A & Gupta K S, unpublished work.
- Aten Jr A W H, Louwrier K P, Coppens P H, Kok H A, de Ross A M, Kriek E, Hillege A, Vollbracht L & Hartog E, *J inorg nucl Chem*, 3 (1956) 296.
- van Eldik R & Harris G M, *Inorg Chem*, 19 (1980) 880.
- Dolgoplosk B A & Tinyakova E I, *Redox systems as sources of free radicals* (Moscow) 1972.
- Lezina G G, Lunenok-Burmakina V A, Emelyanov V B & Rubanik S K, *Russian J inorg Chem*, 23 (1978) 457.
- Wilmarth W K & Haim A, *Peroxide oxidation mechanisms*, edited by J O Edwards (Interscience, New York) 1962 p 186.
- Neta P, Huie R E & Ross A B, *J phys Chem Ref Data*, 17 (1988) 1142.
- Isied S & Taube H, *Inorg Chem*, 13 (1974) 1545.
- Olson T M, Boyce S D & Hoffmann M R, *J phys Chem*, 90 (1986) 2482.