Kinetics and Mechanism of Oxidation of Dimethyl Sulfoxide by Peroxomonosulfate

Thanthoni PANDURENGAN and Pichai MARUTHAMUTHU*
Department of Chemistry, University of Madras, Autonomous post-Graduate Centre,
Tiruchirapalli-620020, India

(Received January 23, 1981)

The kinetics of oxidation of dimethyl sulfoxide (DMSO) by peroxomonosulfate (PMS) was carried out in aqueous H_2SO_4 medium (0.1—0.5 M $H^{+\dagger}$) and in buffered media, pH=4.6 and 7.0, at temperatures, 10 and 20 °C. The reaction obeys a total second order kinetics, first order each with respect to [PMS] and [DMSO]. The rate was found to be immeasurably fast at pH≥9 and T>20 °C. In strong acid medium, $[H_2SO_4]=0.1—0.5$ M, the reaction was found to follow an inverse first order dependence on $[H^+]$. The rate law for the disappearance of PMS is found to be

$$\text{Rate} = \{k_a + k_b[H^+]^{-1}\}[\text{PMS}][\text{DMSO}]$$

indicating both the acid-independent and inverse acid-dependent reactions occurring concurrently. Dimethyl sulfone was identified as the oxidation product and the reaction stoichiometry, [DMSO]:[PMS] was found to be 1:1. The kinetic and thermodynamic parameters evaluated strongly suggest the nucleophilic substitution mechanism characteristic of peroxides. A comparison is also made with the corresponding reactions of the similar peroxides, H_2O_2, $S_2O_8{}^{2-}$, $P_2O_8{}^{4-}$, and $H_2PO_5{}^-$.

There are many investigations on the oxidation of organic and inorganic compounds by the well-known oxidant, peroxodisulfate,[1,2] $S_2O_8{}^{2-}$, whereas the corresponding monoperoxo compound, namely peroxomonosulfate, $HSO_5{}^-$ has received relatively little attention despite the fact that it is known to chemists nearly a century ago.[3] Peroxomonosulfate can be regarded as mono substituted hydrogen peroxide in which one of the hydrogens is replaced by a SO_3 group. Metal ion catalysed[4] and uncatalysed[5] thermal decomposition of peroxomonosulfate (PMS) and oxidation of chloride and halide[6] and nitrite[7] ions have already been carried out by Edwards and coworkers. Recently radiolytic chain decomposition[8] and oxidation of azide, azidopentamminechromiun(III)[9] and tris(2,2′-bipyridine)iron(II)[10] by peroxomonosulfate have been carried out. It has been observed that peroxomonosulfate is a better oxidant than peroxodisulfate in the reaction with halide ions.

It was the intention of the authors to utilize peroxomonosulfate in the oxidation reaction of various substrates to explore the possibility of its synthetic utility. As a part of this goal, dimethyl sulfoxide, which is emerging not only as a solvent but also as a versatile reagent, was chosen as the substrate for the present investigation to find out the ease with which an aprotic solvent is oxidized by peroxomonosulfate. In general, peroxoacids[11,12] are found to be effective oxidants in bringing about the oxidation of sulfides and sulfoxides. In the reactions of sulfides, it is inferred that the nucleophilic attack is made by the sulfur of sulfides on the peroxo oxygen of the oxidant and the reverse was found to be true in the case of sulfoxides. Peroxomonosulfate may resemble either peroxodisulfate (free radical mechanism) or organic peroxides (ionic mechanism) in its reactions. The present investigation focuses attention on (i) the kinetics of the reaction with the concurrent effect of pH and high acidity since the peroxides are prone to acid-catalysis (ii) mechanistic aspects with the kinetic and thermodynamic reasoning and (iii) the comparative behaviour of PMS with those of H_2O_2, $S_2O_8{}^{2-}$, $P_2O_8{}^{4-}$, and peroxomonophosphate, $H_2PO_5{}^-$, in effecting the oxidation of DMSO.

Experimental

All the chemicals used were of analar grade. Potassium peroxomonosulfate was donated by Du Pont Chemical Co., U.S.A. under the trade name "oxone." It is a triple salt with the composition $2\,KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$. The purity of this salt was estimated by cerimetry using ferroin indicator, as well as by iodometry and was found to be 96% pure. Tests with permanganate showed the absence of free hydrogen peroxide. No attempt was made to further purify this compound because all previous attempts have been reported unsuccessful.[8] From the methods of preparation of this compound, it is assumed that $KHSO_4$ or K_2SO_4 or both might account for the 4% difference between the formula and the analysis results[8]. Other chemicals such as dimethyl sulfoxide (Fluka), KI, $Na_2S_2O_3 \cdot 5H_2O$, NaH_2PO_4, Na_2HPO_4, CH_3COOH, and CH_3COONa (BDH) were all analytical grade samples. Perchloric acid (60%) was from E. Merck and all these chemicals were used as such.

Experiments were carried out in buffered media, pH 4.6 and 7, and in acidic medium provided by 0.1 to 0.5 M H_2SO_4. In buffered media, it was always necessary to use a high concentration of the buffer (0.1 M) since the product, $HSO_4{}^-$, is a stronger acid than the oxidant, $HSO_5{}^-$. Under the present experimental conditions, no spontaneous self-decomposition of peroxomonosulfate, even up to pH 12, was observed. The kinetics of the reaction was followed by estimating the amount of peroxomonosulfate disappeared by iodometry at different time intervals. The rate constants were obtained using integral method. The stoichiometry of the reaction was determined by taking a known excess concentration of peroxomonosulfate over dimethyl sulfoxide and allowing the reaction to completion at room temperature (30 °C). Different concentrations of DMSO (0.01—0.04 M) and PMS (0.02—0.08 M) were taken and after the reaction was over, the remaining PMS was estimated by iodometry. The stoichiometry of the reaction, [DMSO]:[PMS] in all the concentration range studied, was found to be 1:1. The only product of the reaction was identified to be dimethyl sulfone, a white solid, mp 109 °C;

---

† 1 M=1 mol dm^{-3}.

IR: $\nu_{S=O}$ at 1310 and 1140 cm^{-1}, characteristic of sulfones. The error limits of the kinetic constants were calculated by the method of least squares. Duplicate experiments were carried out to check the reproducibility of the results and it was found that the results were reproducible within the error of ±5%.

Results and Discussion

All the experiments were carried out under pseudo-first-order conditions with [DMSO] at least ten times higher than that of PMS. The experiments could be done only at two different temperatures, 10 and 20 °C, and at higher temperatures, the reaction was found to be immeasurably fast. Plots of log $[\mathrm{PMS}]_t$ *versus* time/min (Fig. 1) were found to be linear showing a first-order dependence on [PMS]. The pseudo-first-order rate constants, k'/s^{-1}, evaluated from the slopes of the above plots were found to be independent of the initial concentration of PMS (Fig. 1), further confirming the first-order dependence on [PMS]. The plots of log $[\mathrm{PMS}]_t$ *vs.* time at different initial concentrations of DMSO and at a fixed concentration of PMS were found to be linear (Fig. 2) and the pseudo-first-order rate contants, k', evaluated from these plots were found to increase with increase in [DMSO]. Plots of k' *vs.* [DMSO] were found to be linear passing through origin (Fig. 3) showing a first-order dependence with respect to [DMSO] also. From the slopes of the above plots, the second-order rate constants, k_2 (dm^3 mol^{-1} s^{-1}), were evaluated. In acid medium (H_2SO_4), the values of k_2 were found to decrease with increase in [H$^+$] (0.1—0.5 M) and the plot of k_2 *vs.* [H$^+$] was found to be linear with negative slope showing an inverse first-order dependence on [H$^+$] and consequently the plot of k_2 [H$^+$] *vs.* [H$^+$] was linear with intercept on the ordinate (Fig. 4). The variation of pH from 4.6 to 7 was found to increase the rate (Table 1) and the reaction at pH≥9 was found

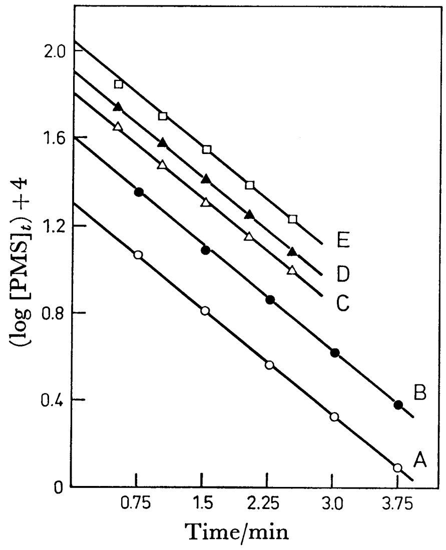


Fig. 1. First-order kinetics in [PMS]. pH=4.6; μ=0.12 M, T=20 °C; [DMSO]=0.125 M; [PMS]=2,4,6,8,10×10^{-3} M (A—E).

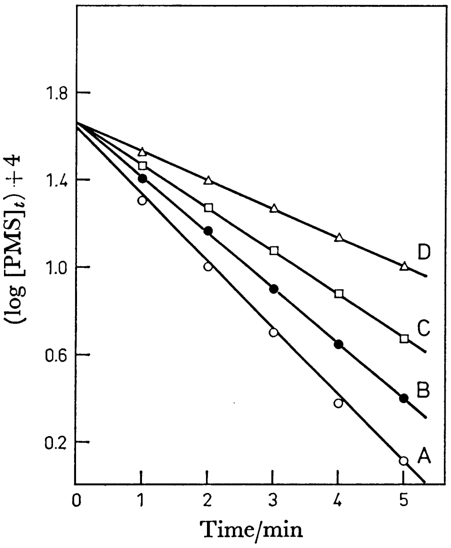


Fig. 2. Evaluation of pseudo-first-order rate constants at different [DMSO]. pH=4.6; μ=0.12 M; T=20 °C; [PMS]=4.3×10^{-3} M; [DMSO]=5,7.5,10,12.5×10^{-2} M (A—D).

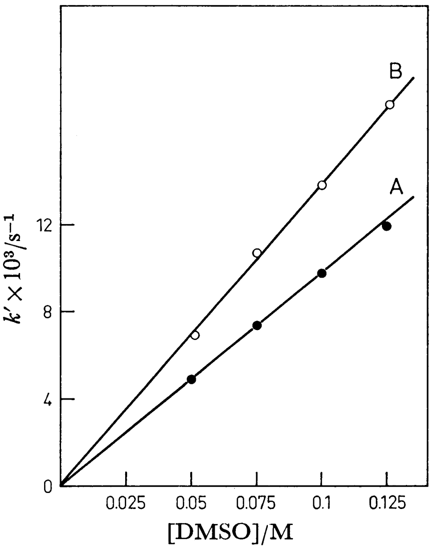


Fig. 3. First-order dependence on [DMSO]. plot A: pH 4.6; plot B: pH=7.0; μ=0.12 M; T=20 °C.

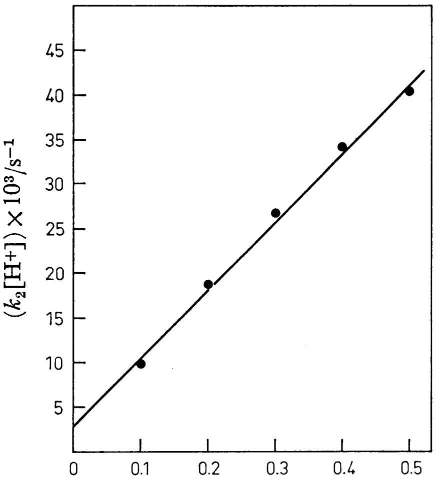


Fig. 4. Effect of [H$^+$] on k_2. μ=0.6 M; T=20 °C.

Table 1. Kinetic and thermodynamic parameters

pH	T °C	$k_2\times10^2$ $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$	E_a $\mathrm{kJ\,mol^{-1}}$	ΔH^* $\mathrm{kJ\,mol^{-1}}$	ΔS^* $\mathrm{J\,deg^{-1}\,mol^{-1}}$	ΔG^* $\mathrm{kJ\,mol^{-1}}$
4.6	10	4.80	50.2	47.7	−101.7	77.5
	20	9.90				
7.0	10	6.91	45.6	43.1	−114.7	77.5
	20	13.36				
0.3MH+	10	4.93	40.2	37.7	−146.1	80.8
	20	8.83				

to take place instantaneously and consequently no experiment was done at pH>7. The presence or absence of atmospheric oxygen was found to have no effect on the reaction rate. Added acrylonitrile monomer was found to polymerize in deaerated reaction systems containing (i) acrylonitrile and PMS and (ii) acrylonitrile, PMS, and DMSO when [DMSO]≤[PMS]. However, when the concentration of DMSO was increased to greater than ten times that of PMS, complete suppression of polymerization occurred and consequently no polymer formation was observed. This indicates that at low concentrations of DMSO and in the absence of it, the polymer formed was only due to the direct reaction between PMS and acrylonitrile and not due to the formation of any radical intermediate in the reaction between DMSO and PMS. The absence of any radical intermediate was also confirmed ESR by experiments.[13] DMSO and PMS were mixed in the ESR cavity in a flow system[14] and the ESR measurements were taken. No ESR signal corresponding to any radical species could be seen. Since peroxomonosulfate would give rise to $\cdot\mathrm{OH}$ and $\dot{\mathrm{S}}\mathrm{O}_4^-$ by homolytic scission and $\dot{\mathrm{S}}\mathrm{O}_4^-$ and OH^- or $\dot{\mathrm{O}}\mathrm{H}$ and SO_4^{2-} with reducing agents,[10] such very reactive radical species, if they are formed, would have produced radicals such as $\dot{\mathrm{C}}\mathrm{H}_3$[15] from DMSO. Experiments were also conducted by mixing PMS solution and that of DMSO containing fumaric acid in the flow system and ESR signals were looked for. Since fumaric acid is an efficient spintrapping agent[16–18] for $\dot{\mathrm{O}}\mathrm{H}$, $\dot{\mathrm{S}}\mathrm{O}_4^-$, and organic radicals, absence of any ESR signal confirms positively the absence of radicals as the intermediate in the PMS–DMSO system.

Peroxomonosulfuric acid ($\mathrm{HO{-}OSO_3H}$) has two ionisable protons. Strictly speaking, one is the sulfuric acid proton and the other is the hydrogen peroxide proton. The pK_a value of the sulfuric acid proton lies in a high acidity region and that of hydrogen peroxide proton[4] is 9.4. Since the rate was found to be increased enormously as the pH is increased and decreased as [H+] was increased and also from the nature of $k_2[\mathrm{H^+}]$ *vs.* $[\mathrm{H^+}]$ plot leaving intercept on the ordinate (Fig. 4), the following mechanism of oxidation involving acid-independent and inverse acid-dependent paths may be proposed.

$$\mathrm{HO{-}O{-}SO_3^-} \overset{K}{\rightleftharpoons} \mathrm{{}^-O{-}O{-}SO_3^-} + \mathrm{H^+} \tag{1}$$

$$\mathrm{(CH_3)_2SO} + \mathrm{HO{-}OSO_3^-} \xrightarrow{k_a} \mathrm{(CH_3)_2SO_2} + \mathrm{SO_4^{2-}} + \mathrm{H^+} \tag{2}$$

$$\mathrm{(CH_3)_2SO} + \mathrm{{}^-O{-}O{-}SO_3^-} \xrightarrow{k_b} \mathrm{(CH_3)_2SO_2} + \mathrm{SO_4^{2-}} \tag{3}$$

The rate equation for the disappearance of PMS is given as

$$\mathrm{Rate} = \frac{-\mathrm{d[PMS]}}{\mathrm{d}t} = k_a[\mathrm{DMSO}][\mathrm{HSO_5^-}] + k_b[\mathrm{DMSO}][\mathrm{SO_5^{2-}}] \tag{4}$$

$$= k_a[\mathrm{DMSO}][\mathrm{HSO_5^-}] + \frac{k_bK[\mathrm{DMSO}][\mathrm{HSO_5^-}]}{[\mathrm{H^+}]} \tag{5}$$

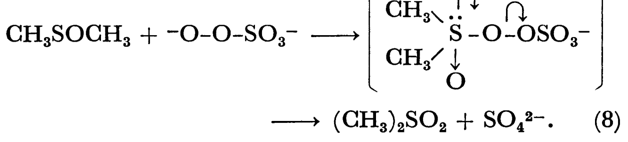
$$\frac{\mathrm{Rate}}{[\mathrm{DMSO}][\mathrm{PMS}]} = k_2 = k_a + k_bK[\mathrm{H^+}]^{-1}, \tag{6}$$

where k_2 is the overall second-order rate constant and k_a and k_b are acid-independent and inverse acid-dependent rate constants respectively. Equation 6 may be rearranged into a convenient form,

$$k_2[\mathrm{H^+}] = k_a[\mathrm{H^+}] + k_b[\mathrm{K}]. \tag{7}$$

Using the rate constants at $[\mathrm{H^+}]=0.1$—$0.5\,\mathrm{M}$, the plot of $k_2[\mathrm{H^+}]$ *vs.* $[\mathrm{H^+}]$ was drawn (Fig. 4). From the line of best fit, the value of $k_a=7.70\times10^{-2}\,\mathrm{M^{-1}}$ was obtained as the intercept. From the slope of the above plot, k_bK, the value of $k_b=7.37\times10^6\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ was obtained using the literature value[4] of $K=3.98\times10^{-10}$. It is seen that k_b is approximately eight orders of magnitude higher than k_a. So, it is not surprising that the reaction between DMSO and PMS is instantaneous at pH>9 where PMS exists as $\mathrm{{}^-O{-}O{-}SO_3^-}$. This also points to the fact that the reaction occurs predominantly with $\mathrm{SO_5^{2-}}$ as the active species of PMS. In general, the reactions of peroxide are prone to acid-catalysis. The present investigation is interesting in that an inverse acidity dependence is observed. The higher reactivity of $\mathrm{SO_5^{2-}}$ than that of $\mathrm{HSO_5^-}$ may be considered to be in favour of a nucleophilic attack by the peroxide.

The foregoing kinetic results, second-order kinetics and inverse acidity dependence, may suggest a nucleophilic substitution mechanism on the sulfur atom in DMSO by PMS as shown below.



$$\mathrm{CH_3SOCH_3} + \mathrm{{}^-O{-}O{-}SO_3^-} \longrightarrow \left[\begin{array}{c}\mathrm{CH_3}\\ \end{array}\!\!\begin{array}{c}\mathrm{S{-}O{-}OSO_3^-}\\ \downarrow\\ \mathrm{O}\end{array}\right] \longrightarrow \mathrm{(CH_3)_2SO_2} + \mathrm{SO_4^{2-}}. \tag{8}$$

A similar mechanistic behavior involving the nucleophilic attack of peroxide oxygen on the sulfur atom of sulfoxide has been observed in the oxidation of diphenyl sulfoxide by perbenzoic acid.[12] There is also abundant evidence that peroxo anions are strongly nucleophilic as pointed out in earlier work.[19] The kientic and thermodynamic parameters, for the present investigation, calculated by using standard equations are presented in Table 1. The thermodynamic parameters given are for the overall second-order rate constants, k_2, obtained only at two temperatures, 10 and 20 °C because the reaction was immeasurably fast above 20 °C. Nevertheless the values of activation parameters,

$$\Delta H^* = 37.7 \text{ to } 47.7 \text{ kJ mol}^{-1} \quad \text{and}$$

$$\Delta S^* = -101.7 \text{ to } -146.1 \text{ J deg}^{-1}\text{mol}^{-1}$$

observed by us, are of the same order of magnitude as observed by Edwards[20] for typical nucleophilic second-order reactions,

$$\Delta H^* = 37.7 \text{ to } 71.2 \text{ kJ mol}^{-1} \quad \text{and}$$

$$\Delta S^* = -41.9 \text{ to } -146.5 \text{ J deg}^{-1}\text{mol}^{-1}.$$

Comparison with the oxidation of sulfoxides by other inorganic peroxides:

Oxidations[12,20,21] of sulfides and sulfoxides by hydrogen peroxide and organic peroxoacids, are discussed in terms of nucleophilic reactions. In general, the reactions follow a second order rate law, first order each with respect to [peroxoacid] and [reductant]. In the case of sulfides, the nucleophilic attack on peroxo oxygen is made by sulfur of the sulfide and the reverse was found to be true in the case of sulfoxides.[12] The kinetic and thermodynamic parameters are found to be consistent with the mechanistic reasonings for an S_N2 mechanism.

Peroxodisulfate oxidation of DMSO has not been carried out so far. But from the available data[22,23] on the sulfoxides, such as diethyl and diphenyl sulfoxides, it can be understood that the oxidation rates at low concentrations of sulfoxides follow a total first order kinetics, first order with respect to $[S_2O_8^{2-}]$ and zero order with respect to [sulfoxide] and a total second order, first order each with respect to $[S_2O_8^{2-}]$ and [sulfoxide] at higher concentrations of sulfoxide. From the observation that oxygen does not affect the rate of the diethyl sulfoxide–$S_2O_8^{2-}$ reaction, Howard and Levitt[18,19] suggested that the reactions do not proceed by a free radical mechanism. But it is argued[2] that the increase in the rate of disappearance of peroxodisulfate ion in the presence of sulfoxide and the zero order dependence upon sulfoxide concentration would indicate that a chain reaction is operative.

The kinetics and mechanism of oxidation of dimethyl sulfoxide by peroxodiphosphate[24] was carried out recently. It was found that the reaction was strongly acid-catalysed. The reaction obeys a total first order, first order with respect to the [oxidant] and zero order with respect to [DMSO]. The kinetic data are rationalised by a free radical chain mechanism. Dimethyl sulfone was identified to be the sole product of oxidation, the stoichiometric reaction being

$$(CH_3)_2SO + H_3P_2O_8^- + H_2O \longrightarrow (CH_3)_2SO_2 + 2H_2PO_4^- + H^+. \qquad (9)$$

The energy of activation for the reaction is 75.8 kJ mol^{-1} which is lower than the –O–O– bond energy of the peroxide. Comparison of the data on the oxidation of water by peroxodiphosphate indicated that the aprotic solvent, DMSO, was oxidised with more facility than the protic solvent, H_2O.

The kinetics of oxidation of dimethyl sulfoxide by peroxomonophosphate,[25] $H_2PO_5^-$, the phosphorus analog of peroxomonosulfate, was found to follow the similar rate law as in the present investigation except for the acid-dependence. The reaction is found to obey a second order kinetics, first order each with respect to [DMSO] and $[H_2PO_5^-]$. The reaction shows a direct first-order dependence on $[H^+]$ in strong acid (H_2SO_4) medium and the rate decreases with increase in pH in buffered media. This acid-dependence is in sharp contrast to that found in the present investigation wherein an inverse acidity dependence is observed. Comparison of rate constants under similar experimental conditions show that peroxomonosulfate is a more powerful oxidant than peroxomonophosphate and the former oxidant can be used as an analytical reagent to estimate dimethyl sulfoxide at room temperature, provided the estimation is done at alkaline pH.

References

1) D. A. House, *J. Chem. Soc.*, **62**, 185 (1962).

2) W. K. Wilmarth and A. Haim, "Peroxide Reaction Mechansims," ed by J. O. Edwards, Interscience, New York (1962), p. 175.

3) T. S. Price, *J. Chem. Soc.*, **89**, 54 (1906).

4) D. L. Ball and J. O. Edwards, *J. Am. Chem. Soc.*, **78**, 1125 (1956).

5) D. L. Ball and J. O. Edwards, *J. Am. Chem. Soc.*, **62**, 343 (1958).

6) R. W. Johnson and J. O. Edwards, *Inorg. Chem.*, **5**, 2073 (1966); D. H. Fortnum, C. J. Battaglia, S. R. Cohen, and J. O. Edwards, *J. Am. Chem. Soc.*, **82**, 718 (1960).

7) J. O. Edwards and J. J. Müller, *Inorg. Chem.*, **1**, 696 (1962).

8) P. Maruthamuthu and P. Neta, *J. Phys. Chem.*, **81**, 937 (1977).

9) R. C. Thompson, P. Wieland, and E. H. Appleman, *Inorg. Chem.*, **18**, 1974 (1979).

10) R. Somuthevan, R. Renganathan, and P. Maruthamuthu, *Inorg. Chim. Acta Lett.*, **45**, 165 (1980).

11) C. G. Overberger and R. W. Cummins, *J. Am. Chem. Soc.*, **75**, 4250 (1953).

12) H. H. Szmant, H. F. Harnsberger, and F. Krahe, *J. Am. Chem. Soc.*, **76**, 2185 (1954).

13) Experiments conducted by one of the authors (P.M.) at the Max-Planck-Institut für Strahlenchemie, Mülheim (Ruhr), West Germany.

14) B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J. Chem. Soc.*, *Perkin Trans. 2*, **1973**, 2174.

15) B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J. Chem. Soc.*, *Perkin Trans. 2*, **1975**, 303, 308.

16) P. Neta, *J. Phys. Chem.*, **75**, 2570 (1971).

17) Om P. Chawla and R. W. Fessenden, *J. Phys. Chem.*, **79**, 2693 (1975).

18) P. Maruthamuthu and H. Taniguchi, to be published: Fumaric acid was used successfully as an efficient spin-trapping agent to trap $\dot{O}H$ and $\dot{S}O_4^-$ in the photolysis

of aqueous solution of peroxomonosulfate.

19) C. A. Bunton, in Ref. 2, p. 11; W. P. Jencks and J. Carriuolo, *J. Am. Chem. Soc.*, **82**, 1778 (1960).

20) J. O. Edwards, in Ref. 2, p. 67.

21) S. D. Ross, *J. Am. Chem. Soc.*, **68**, 1484 (1946).

22) H. Howard, Jr., and L. S. Levitt, *J. Am. Chem. Soc.*, **75**, 6170 (1953).

23) R. L. Eager and C. A. Winkler, *Can. J. Res.*, **26** (B), 527 (1948).

24) P. Maruthamuthu and M. Santappa, *Ind. J. Chem.* **16A**, 43 (1978).

25) R. Viswamurthy and P. Maruthamuthu, *Oxidation Commun.*, in press.