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Oxidation Studies with Peroxomonophosphoric Acid. III. A Kinetic and Mechanistic Study of Oxidation of Dialkyl Sulfides

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The kinetics of oxidation of dialkyl sulfides by peroxomonophosphate in aqueous medium at 308 K and $\mu=$ 0.4 mol dm^{-3} follow the rate expressions (i) $-\mathrm{d}[\text{peroxomonophosphate}]/\mathrm{d}t=\{k_1[\mathrm{H_2PO_5^-}]+k_2[\mathrm{HPO_5^{2-}}]\}[\text{sulfide}]$ in the pH region 6.8—8.7 where k_1 and k_2 values are 336.5 and 0.95, 69.7 and 0.254, and 27.5 and 0.126 dm^3 mol^{-1} s^{-1} for dimethyl, diethyl and dipropyl sulfides, respectively, (ii) $-\mathrm{d}[\text{peroxomonophosphate}]/\mathrm{d}t=k_2[\mathrm{HPO_5^{2-}}]\cdot[\text{sulfide}]$ in the pH region 8.5—12.5, where the average k_2 values are 0.86, 0.247, and 0.128 dm^3 mol^{-1} s^{-1} for dimethyl, diethyl, and dipropyl sulfides, respectively, and (iii) $-\mathrm{d}[\text{peroxomonophosphate}]/\mathrm{d}t=\{k_2[\mathrm{HPO_5^{2-}}]+k_3\cdot[\mathrm{PO_5^{3-}}]\}[\text{sulfide}]$ in the pH region 12.5—13.7, the k_2 and k_3 values being 0.947 and 0.107, and 0.233 and 0.018 dm^3 mol^{-1} s^{-1} for dimethyl, and diethyl sulfides, respectively. The mechanism of the reaction is in line with a nucleophilic attack of the sulfide-sulfur on the peroxo oxygen, giving rise to S_N 2-type transition states which undergo oxygen–oxygen bond fission to give the corresponding sulfoxide and phosphate.

Organic sulfides have been oxidised[1–14] by various peroxo compounds. Howard and Levitt[6] pointed out that in the oxidation of diethyl sulfide by persulfate at pH 8 the reaction sequence should be sulfide→sulfoxide→sulfone, the second step of oxidation of the sulfoxide to sulfone being very slow. Electrophilic nature of the peroxo oxygen in this oxidation was suggested.

Curci and Modena[11,12] carried out studies on the steric and polar influences on peroxide oxidation rates of organic sulfides. In the oxidation of methyl phenyl sulfides and diphenyl sulfides by $\mathrm{H_2O_2}$ in acidic ethanol solution,[8] the nucleophilic nature of the sulfide molecule was well established. Modena[9] observed the effects of alkyl group structure in alkyl phenyl sulfides, alkyl benzyl sulfides being predominantly steric.

Various reports have appeared on the oxidation of organic sulfides by peroxo compounds. However, no work seems to have been carried out on the oxidation of sulfides by peroxomonophosphoric acid. In continuation of our work[15,16] on the oxidation of organic substrates by peroxomonophosphoric acid in acid and alkaline pH, we are reporting the study on the oxidation of dialkyl sulfides by peroxomonophosphoric acid.

The oxidation was studied over the pH range 6—14, contribution of the various peroxomonophosphoric acid species being estimated. It is of interest that the pH dependence of the oxidation rate is quite contrary to that observed in the dimethyl sulfoxide oxidation.[16]

Experimental

All the chemicals were of AnalaR grade. Peroxomonophosphoric acid (PMPA) was prepared by the acid hydrolysis[17–20] of potassium peroxodiphosphate. Perchloric acid, used for hydrolysis, was neutralised by addition of a requisite amount of sodium hydroxide. The ionic strength of the medium was maintained with sodium perchlorate. The pH of the solution, adjusted with standard buffers or carbonate-free hydroxide, was determined with a Systronics digital pH-meter 335. Reactions were followed by measuring the rate of disappearance of peroxomonophosphoric acid, the estimation of which was made in an acetic acid–acetate buffer at a pH≈ 4—5 with a drop of ammonium molybdate solution (to avoid the diffused end point due to the presence of 2—3% of $\mathrm{H_2O_2}$ formed during the course of hydrolysis) by the usual iodometric procedure. The self-decomposition of peroxomonophosphate (PMP), which occurs to some extent in the presence of higher [OH$^-$] due to

$$\mathrm{PO_5^{3-}} \longrightarrow \mathrm{PO_4^{3-}} + 1/2\mathrm{O_2}$$

was found to be either nil or negligibly small. However, in a few cases, due allowance has been made to account for the self decomposition of the oxidant.

Results and Discussion

The kinetics of oxidation of dialkyl sulfides by PMP in alkaline pH have been investigated at 308 K. Kinetic runs with PMP in the range 2.91—9.26×10^{-4} mol dm^{-3} in the presence of excess [sulfide] at fixed pH and μ show a first-order disappearance of PMP. This follows from the constancy of the first-order rate constants (k_1') up to at least 60% completion of the reaction with respect to the disappearance of PMP in any single run when [sulfide]>[PMP].

The oxidation also exhibits a first order dependence on [sulfide] as seen from the constancy of the second-order rate constants k_2' (Table 1), calculated either by: $k_2'=k_1'/[\text{sulfide}]$ (when [sulfide]>[PMP]) or from the usual second-order rate expression (when [sulfide]≈[PMP]).

The variation of ionic strength using $\mathrm{NaClO_4}$ was found to have negligible effect on the oxidation rate, indicating the rate determining slow step to involve at least one neutral molecule.[21] The oxidation rate is insensitive to the addition of acrylamide, indicating the absence of radicals in the reaction system.

Temperature dependence in the range 298—318 K for different dialkyl sulfides at pH 13.01 is given in Table 1. Activation parameters have been evaluated from the linear Arrhenius plots of $\log k_2'$ *vs.* T^{-1} (Table 2).

The influence of pH on oxidation rate has been studied in the pH ranges 7.36—13.7 for dimethyl sulfide, 6.76—13.7 for diethyl sulfide, and 6.87—13.0 for dipropyl sulfide. The results are interesting. Plots of pH *vs.* $\log k_\mathrm{obsd}(=\log k_2')$ for different dialkyl sulfides are shown in Fig. 1. The plots in sigmoid form suggest the participation of various species of PMP in the oxidation. The pH $-\log k_\mathrm{obsd}$ plots can be

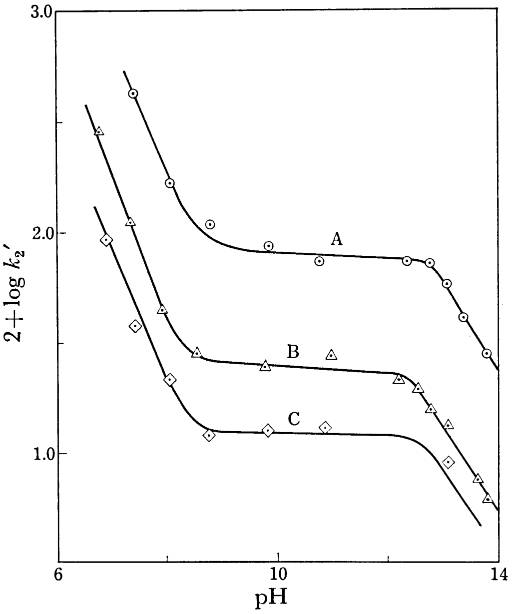


Fig. 1. Plots of log k_2' *vs.* pH (pH range 6.8 to 13.7).
A: Dimethyl sulfide, B: diethyl sulfide, C: dipropyl sulfide.

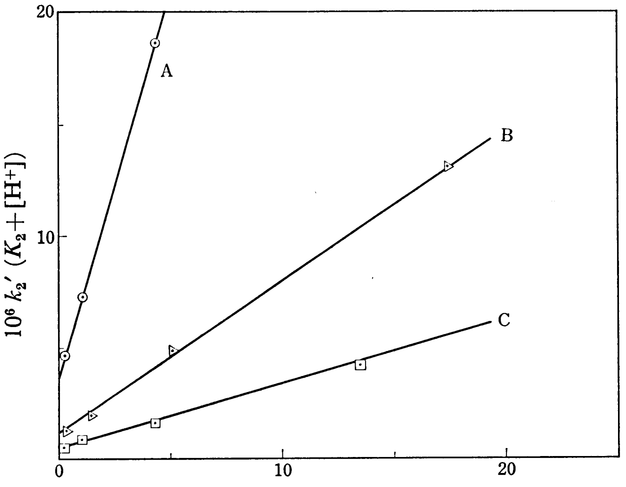


Fig. 2. Plots of k_2' $(K_2+[H^+])$ *vs.* $[H^+]$ (pH range 6.8 to 8.7).
A: Dimethyl sulfide, B: diethyl sulfide, C: dipropyl sulfide.

divided into three distinct pH regions 6.8—8.7, 8.7—12.5, and 12.5—13.7. The oxidation rate in the case of sulfides decreases with increasing $[OH^-]$, quite contrary to the oxidation of dimethyl sulfoxide by PMP where the rate increases with the increasing $[OH^-]$ (Table 3).[16)]

Various equilibria[19)] involving peroxomonophosphoric acid in solution are:

$$H_3PO_5 \xrightleftharpoons{K_1} H_2PO_5^- + H^+ \qquad (1)$$

$$H_2PO_5^- \xrightleftharpoons{K_2} HPO_5^{2-} + H^+ \qquad (2)$$

$$HPO_5^{2-} \xrightleftharpoons{K_3} PO_5^{3-} + H^+ \qquad (3)$$

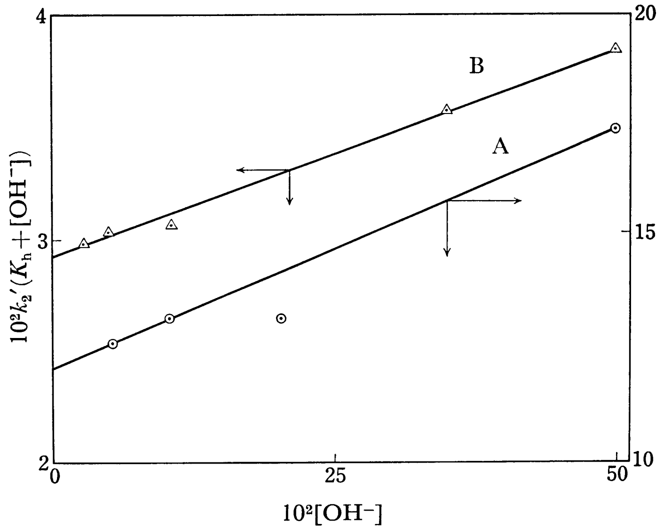


Fig. 3. Plots of k_2' $(K_h+[OH^-])$ *vs.* $[OH^-]$ (pH range 12.5 to 13.7).
A: Dimethyl sulfide, B: diethyl sulfide.

The dissociation constants, K_1, K_2, and K_3 are 8.0×10^{-2}, 4.2×10^{-6}, and 1.6×10^{-13}, respectively[19)] at 298 K and $\mu=0.2$ mol dm^{-3}.

Since the species H_3PO_5, $H_2PO_5^-$, HPO_5^{2-}, and PO_5^{3-} become predominant with increasing pH in the order specified and the electrophilic character of these species decreases, it is evident from the pH dependence of the sulfide oxidation that the rate of oxidation decreases with decreasing electrophilic character of PMP species. A reverse trend has been observed in the case of DMSO oxidation[16)] by PMP in the pH range 10—13.6; this has been rationalised on the basis of a nucleophilic attack of the PMP species on the sulfur of the sulfoxide.

The oxidation rate decreases in the order: dimethyl> diethyl>dipropyl sulfide. This could be attributed to the steric factor rather than to the polar effects which arises from the fact that in the oxidation[9)] of alkyl phenyl sulfides and alkyl benzyl sulfides the effect of alkyl group structure is postulated to be predominantly steric. Although it is hard to sort out the polar and steric effects in the case of the dialkyl sulfides, the rate enhancement observed by the electron-releasing substituents on the aromatic rings of the alkyl phenyl sulfides is in the expected order of reactivity for the sulfide acting as a nucleophile.

On the other hand peroxides acting as electrophiles are not uncommon;[22,23)] the observed second-order kinetics, the high negative entropies of activation and catalysis by acid support the electrophilic nature of the peroxide.

The sulfide molecule can be envisaged to participate in a nucleophilic attack on the peroxo oxygen, giving rise to the corresponding sulfoxide which does not undergo further oxidation. This arises from the fact that (i) TLC-analysis of the reaction mixture after about 80% completion of the reaction with respect to the consumption of PMP does not show the presence of any sulfone, and (ii) the rate of oxidation of dimethyl sulfoxide[16)] is much lower than that of the dimethyl

TABLE 1.$^{a)}$ OXIDATION OF DIALKYL SULFIDES BY PEROXOMONOPHOSPHATE

Sulfide	10^3 [sulfide] / mol dm^{-3}	10^4[PMP] / mol dm^{-3}	pH	$10^2k_2'^{b)}$ / dm^3 mol^{-1} s^{-1}	$10^2k_2'$ Calcd / dm^3 mol^{-1} s^{-1}
Dimethyl sulfide	2.65	3.63	13.01	57.8	
	5.31	3.42	13.01	65.0	
	1.91	4.89	13.01	58.1	
	1.75	4.69	13.01	58.7$^{c)}$	
	2.09	4.69	13.01	29.7$^{d)}$	
	2.09	4.62	13.01	36.5$^{e)}$	
	1.54	4.26	13.01	74.1$^{f)}$	
	1.75	4.44	13.70	27.8$^{g)}$	27.4
	1.78	3.30	13.30	40.4	42.8
	1.91	4.89	13.01	58.1	56.7
	1.78	4.49	12.72	71.5	69.9
	1.46	3.64	12.30	73.0	
	2.15	3.80	10.71	73.8	
	2.15	4.00	9.77	87.8	
	2.12	4.63	8.74	111	110
	2.12	4.36	8.00	174	175
	2.18	4.29	7.36	441	440
Diethyl sulfide	1.67	9.26	13.01	14.6	
	1.67	2.91	13.01	14.9	
	1.77	4.54	13.01	13.3	
	0.59	4.54	13.01	13.4	
	1.06	3.76	13.01	12.9	
	2.12	3.76	13.01	13.5	
	1.43	3.99	13.01	17.2$^{h)}$	
	1.43	4.01	13.01	14.9$^{i)}$	
	1.75	5.13	13.01	9.6$^{d)}$	
	1.75	5.20	13.01	11.9$^{e)}$	
	1.93	4.80	13.01	18.9$^{f)}$	
	1.83	4.64	13.70	6.1$^{g)}$	6.1
	1.83	5.53	13.54	7.5	7.5
	1.77	4.54	13.02	13.3	13.5
	1.81	3.81	12.69	17.4	17.3
	1.63	4.49	12.45	19.4	19.3
	1.63	4.78	12.11	21.5	
	1.76	3.73	10.87	28.4	
	1.76	4.54	9.74	24.9	
	1.64	3.84	8.49	29.5	30.7
	1.64	4.36	7.84	46.1	49.2
	1.51	4.86	7.29	115	109
	1.51	4.67	6.76	300	301
Dipropyl sulfide	0.62	4.92	13.02	9.1	
	0.67	4.70	13.02	10.2$^{f)}$	
	0.67	4.27	13.02	11.6$^{j)}$	
	0.66	3.68	10.80	13.4	
	0.66	4.62	9.77	13.0	
	0.66	4.03	8.69	12.2	13.9
	0.67	3.09	7.97	22.3	19.6
	0.67	3.62	7.37	39.1	40.1
	0.67	4.01	6.87	97.9	97.7

a) In aqueous medium, at 308 K and $\mu=0.4$ mol dm^{-3}. b) Observed second-order rate constant. c) In the presence of acrylamide (1.50×10^{-3} mol dm^{-3}). d) At 298 K. e) At 303 K. f) At 313 K. g) $\mu=0.55$ mol dm^{-3}. h) $\mu=0.15$ mol dm^{-3}. i) $\mu=0.6$ mol dm^{-3}. j) At 318 K.

sulfide under similar conditions (Tables 1 and 3).

Since PMPA exists[19] as $H_2PO_5^-$ and HPO_5^{2-} in the pH range 4—7, the reaction sequence can be presented as

$$R_2S\colon + H_2PO_5^- \xrightarrow{k_1} R_2SO + H_2PO_4^- \quad (4)$$

$$R_2S\colon + HPO_5^{2-} \xrightarrow{k_2} R_2SO + HPO_4^{2-} \quad (5)$$

Table 2.[a] OXIDATION OF DIALKYL SULFIDES BY PEROXOMONOPHOSPHATE (Thermodynamic parameters).

Sulfide	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J K^{-1} mol^{-1}
Dimethyl sulfide	44.6	−105
Diethyl sulfide	33.1	−153
Dipropyl sulfide	16.6	−211

a) Calculated at 308 K; in aqueous medium, at μ=0.4 mol dm^{-3} and pH 13.01.

Table 3.[a] OXIDATION OF DIMETHYL SULFOXIDE (DMSO) BY PEROXOMONOPHOSPHATE (PMP)

10^2 [DMSO] mol dm^{-3}	10^4 [PMP] mol dm^{-3}	pH	10^3 k_2'' [b] dm^3 mol^{-1} s^{-1}
5.09	3.23	13.60	23.9[c]
5.09	4.13	13.30	17.9
5.20	2.66	13.03	12.7
5.20	3.45	12.78	8.2
5.09	3.11	12.28	3.7
20.4	4.14	11.55	1.4
20.4	4.06	11.36	0.74
20.4	4.15	11.17	0.59
20.3	4.25	10.88	0.58
20.5	4.29	10.84	0.53
20.3	4.41	10.65	0.40

a) Ref. 16, in aqueous medium at 308 K and μ=0.4 mol dm^{-3}. b) Observed second-order rate constant. c) At μ=0.45 mol dm^{-3}.

The reaction sequence in the pH range 12—14 in which PMP exists[19] as HPO_5^{2-} and PO_5^{3-} would be

$$HPO_5^{2-} + OH^- \xrightleftharpoons{K_4} PO_5^{3-} + H_2O \qquad (6)$$

$$R_2S{:} + HPO_5^{2-} \xrightarrow{k_2} R_2SO + HPO_4^{2-} \qquad (7)$$

$$R_2S{:} + PO_5^{3-} \xrightarrow{k_3} R_2SO + PO_4^{3-} \qquad (8)$$

These equations suggest the rate laws corresponding to pH regions 6.8—8.7 and 12.5—13.7, respectively, as

$$-\mathrm{d}[\text{peroxomonophosphate}]/\mathrm{d}t = \{k_1[H_2PO_5^-]+k_2[HPO_5^{2-}]\}[\text{sulfide}] \qquad (8a)$$

and

$$-\mathrm{d}[\text{peroxomonophosphate}]/\mathrm{d}t = \{k_2[HPO_5^{2-}]+k_3[PO_5^{3-}]\}[\text{sulfide}] \qquad (8b)$$

from which we get:

$$-\frac{\mathrm{d}[\text{PMPA}]}{\mathrm{d}t} = \frac{k_1[H^+]+k_2K_2}{K_2+[H^+]}[\text{PMPA}][\text{sulfide}] \qquad (9)$$

where

$$k_2' = \frac{k_1[H^+]+k_2K_2}{K_2+[H^+]}, \qquad (9a)$$

$$-\frac{\mathrm{d}[\text{PMP}]}{\mathrm{d}t} = \frac{k_2K_h+k_3[OH^-]}{K_h+[OH^-]}[\text{PMP}][\text{sulfide}] \qquad (10)$$

where

$$k_2' = \frac{k_2K_h+k_3[OH^-]}{K_h+[OH^-]} \qquad (10a)$$

and

$$\frac{[H_2O]}{K_4} = K_h \qquad (11)$$

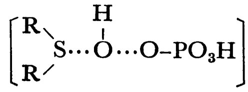
Plots (Fig. 2) of $k_2'\{K_2+[H^+]\}$ against $[H^+]$ (Eq. 9a) in the pH range 6.8—8.7 give straight lines (r=0.999, 0.999, and 0.998 for dimethyl, diethyl, and dipropyl sulfides respectively). From the intercepts and slopes of these least-square plots the values of k_1 and k_2 are respectively calculated to be 336.5 and 0.95 dm^3 mol^{-1} s^{-1} for dimethyl sulfide, 69.7 and 0.254 dm^3 mol^{-1} s^{-1} for diethyl sulfide, and 27.5 and 0.126 for dipropyl sulfide. The second-order rate constants (k_2' calcd) obtained from Eq. 9a with these k_1 and k_2 values, are given in Table 1.

Similarly from Eq. 10a, plots (Fig. 3) of $k_2'\{K_h+[OH^{-1}]\}$ against $[OH^-]$ (with $K_h=K_w/K_3$, where K_w is the ionic product of water and K_3 is the dissociation constant of HPO_5^{2-}) for dimethyl and diethyl sulfides in the pH region 12.5—13.7 are found to be straight lines (r=0.97 and 0.99 respectively). The values of k_2 and k_3 as obtained from the intercepts and slopes of the above plots are respectively 0.947 and 0.107, and 0.233 and 0.018 dm^3 mol^{-1} s^{-1} for dimethyl and diethyl sulfides. With these k_2 and k_3 values, k_2' calcd values have been obtained from Eq. 10a (Table 1).

The k_2 values corresponding to the pH regions 6.8—8.7 and 12.5—13.7 agree excellently with the average k_2' values (0.86, 0.247, and 0.128 for dimethyl, diethyl, and dipropyl sulfides, respectively) in the pH region 8.5—12.5. This leads us to conclude that the PMP species predominantly exists as HPO_5^{2-} in the pH region 8.5—12.5. Thus the oxidation in this pH region can be expressed by

$$-\mathrm{d}[\text{PMP}]/\mathrm{d}t = k_2[HPO_5^{2-}][\text{sulfide}] \qquad (12)$$

The oxidation of dialkyl sulfides by PMP in the pH range 6.8—13.7 can be visualised to involve a nucleophilic attack of the sulfide-sulfur atom on the peroxo-oxygen giving rise to S_N2-type transition states I, II, and III corresponding to steps (4), (5 and 7), and (8) respectively, which undergo oxygen–oxygen bond fission to form the products.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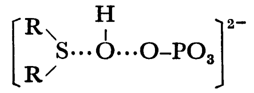
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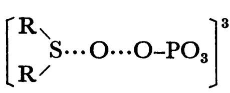
III

This mechanism is in line with the thermodynamic parameters,[7] the magnitude of reactivity of different PMP species and the steric factor[9] involved in the sulfide.

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References

1) L. Lewin, *J. Prakt. Chem.*, **118**, 282 (1928); **119**, 211 (1928); **127**, 77 (1930); **128**, 171 (1930).

2) J. Boeseken and E. Arrias, *Recl. Trav. Chim.*, **54**, 711 (1935).

3) J. Boeseken and A. T. H. Vander Meulen, *Recl. Trav. Chim.*, **56**, 925 (1936).

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

5) C. G. Overberger and R. W. Cummins, *J. Am. Chem. Soc.*, **75**, 4783 (1953).

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

7) L. Bateman and K. R. Hargrave, *Proc. R. Soc. London, Ser. A*, **224**, 389, 399 (1954).

8) G. Modena and L. Maioli, *Gazz. Chim. Ital.*, **87**, 1306 (1957).

9) G. Modena, *Gazz. Chim. Ital.*, **89**, 834 (1959).

10) I. P. Gragerov and A. F. Levitt, *Zh. Obshch. Khim.*, **33**, 543 (1963).

11) R. Curci and G. Modena, *Tetrahedron Lett.*, **25**, 1749 (1963).

12) R. Curci and G. Modena, *Tetrahedron Lett.*, **14**, 863 (1965).

13) R. Curci, F. D. Furia, R. Testi, and G. Modena, *J. Chem. Soc., Perkin Trans. 2*, **1974**, 752.

14) R. Curci, F. D. Furia, and G. Modena, *J. Chem. Soc., Perkin Trans. 2*, **1977**, 576.

15) G. P. Panigrahi and R. S. Panda, *Bull. Chem. Soc., Jpn.*, **52**, 3084 (1979).

16) G. P. Panigrahi and R. S. Panda, *Int. J. Chem. Kinet.*, (in press).

17) D. H. Fortnum, C. J. Battaglia, S. R. Cohen, and J. O. Edwards, *J. Am. Chem. Soc.*, **82**, 778 (1960).

18) C. J. Battaglia, Ph. D. Thesis, Brown University, 1962.

19) C. J. Battaglia and J. O. Edwards, *Inorg. Chem.*, **4**, 552 (1965).

20) F. Secco and M. Venturini, *J. Chem. Soc., Dalton Trans.*, **1976**, 1410.

21) K. J. Laidler, "Chemical Kinetics," Tata McGraw-Hill (1965), p. 229.

22) E. J. Behrman and J. O. Edwards, "Progress in Physical Organic Chemistry," ed by A. Streitwiesser and R. W. Taft, Interscience, New York (1967), Vol. 4, p. 94.

23) J. O. Edwards, "Peroxide reaction mechanisms," ed by J. O. Edwards, Interscience, New York (1962), p. 67.