Kinetics and Mechanism of Oxidation of Aliphatic and Aromatic Ketones by Peroxomonosulphate

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The kinetics of oxidation of ethyl methyl ketone, isobutyl methyl ketone, and acetophenone by peroxomonosulphate (PMS) was carried out in aqueous H_2SO_4 medium (0.20—1.00 mol dm^{-3} H^+) and in aqueous acetic acid medium (40% acetic acid v/v) respectively in the temperature range 30—60 °C at constant ionic strength of 1.20 mol dm^{-3}. The reactions obey total second-order kinetics, first order each with respect to [ketone] and [PMS] for all the ketones. They exhibited acid catalysis with the concurrent occurrence of acid-independent reaction paths conforming to the rate law (i) for the disappearance of

$$-d[\mathrm{PMS}]/dt = k_a[\mathrm{PMS}][\mathrm{ketone}][\mathrm{H}^+] + k_b[\mathrm{PMS}][\mathrm{ketone}] \qquad (i)$$

peroxomonosulphate. The reaction stoicheiometry, [ketone] : [PMS] 1 : 1, for all the ketones indicated the absence of self-decomposition and carbonyl-assisted decomposition of PMS. The kinetic and thermodynamic parameters strongly suggest the mechanism of a fast nucleophilic attack of the oxidant (PMS) on the ketone followed by slow, rate-determining acid-catalysed and uncatalysed decomposition of the intermediate to the product. The reactivity of peroxomonosulphate was compared with those of similar peroxides.

Even though peroxomonosulphate (PMS) has long been known,[1] it has not attracted attention until recently.[2,3] Peroxomonosulphate can be considered as a substituted hydrogen peroxide, replacing one of the hydrogens in H_2O_2 by SO_3. Peroxomonosulphate HSO_5^- is considered to be a precursor of the well known peroxodisulphate $S_2O_8^{2-}$, based on structural similarities. Peroxomonosulphuric acid is a dibasic acid having two ionisable protons, one of them resembling the sulphuric acid proton and the other that of hydrogen peroxide.[2] Kinetic studies involving spontaneous as well as catalytic decomposition of peroxomonosulphate in acidic as well as alkaline media,[2,4] oxidation of halide,[5] nitrite,[6] and chlorite[7] ions have been carried out by Edwards and his co-workers. Radiolytic chain decomposition of peroxomonosulphate and *in-situ* photolytic e.s.r. investigations[8,9] were carried out to identify the species generated by radiolysis and photolysis. Oxidation studies involving azide and azidopentamminechromium-(III),[10] cobalt(II) complexes of aminopolycarboxylic acids,[11] peroxovanadium(V) VO_3,[12] and unsaturated aldehydes[13] have been investigated. Detailed oxidation kinetics of tris-(1,10-phenanthroline)iron(II) sulphate and tris-(2,2′-bipyridyl)iron(II) sulphate,[14] hypophosphite,[15] dimethyl sulphoxide,[16] glycine,[17] anilines[18] by peroxomonosulphate and photochemical chain decomposition and peroxomonosulphate in the presence and absence of propan-2-ol[19] were studied by Maruthamuthu and his co-workers. The kinetics and mechanism of the oxidation of pyridine by Caro's acid (peroxomonosulphuric acid) catalysed by ketones[20] and epoxidation of alkenes by dioxirane intermediates generated in the reaction of potassium caroate with ketones[21] have also been reported.

The treatment of ketones with peroxo compounds gives esters by 'insertion of oxygen'.[22] This best known and most widely studied carbon to oxygen rearrangement is the Baeyer–Villiger reaction.[23] Friess,[24] Friess and Farnham,[25] Friess and Soloway,[26] Doering and Speers,[27] and Doering and Dorfman[28] have studied the mechanism of the Baeyer–Villiger reaction and noted the migratory aptitude of several unsymmetrical ketones with peracetic or perbenzoic acids. Studies of the Baeyer–Villiger reaction of various alkyl and aryl ketones with trifluoroperacetic acid were also made.[29a,b]

The standard electrode potential of peroxomonosulphate is 1.82 V for reaction (1).[30] This high potential suggests the

$$HSO_5^- + 2H^+ + 2e^- \longrightarrow HSO_4^- + H_2O \qquad (1)$$

feasibility of many room-temperature oxidations with peroxomonosulphate. Kennedy and Stock[3] have proved the synthetic utility of peroxomonosulphate with many organic compounds with different functional groups. However, detailed kinetic studies have not been carried out to probe the mechanistic aspects of these reactions. Investigations on the reactions of aliphatic and aromatic aldehydes by peroxomonosulphate[31a,b] revealed the formation of products by migration of aryl and hydride groups in the case of aromatic aldehydes and simple oxidation products in the case of aliphatic aldehydes. It was the intention of the authors to utilize peroxomonosulphate in the oxidation reactions of various substrates to investigate the kinetics and mechanism of reactions. As a part of this goal, the present investigation focuses attention on the reaction of peroxomonosulphate with some representative aliphatic and aromatic ketones.

Experimental

All the chemicals used were of AnalaR grade. Potassium peroxomonosulphate was donated by du Pont de Nemours, under the trade name 'Oxone'.[32] It is a granular, free flowing powder which is a triple salt with the composition $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$. Iodometric and cerimetric measurements[8] were performed to determine its purity and it was found to be 96% pure. The absence of free hydrogen peroxide was confirmed by tests with potassium permanganate. No attempt was made to purify this compound further because of previously unsuccessful attempts.[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 analytical results. Other chemicals such as ethyl methyl ketone, isobutyl methyl ketone, acetophenone, KI, $Na_2S_2O_3 \cdot 5H_2O$, and H_2SO_4 were of analytical grade. Sodium perchlorate was from Merck. Acetic acid was purified following the standard procedure.[33]

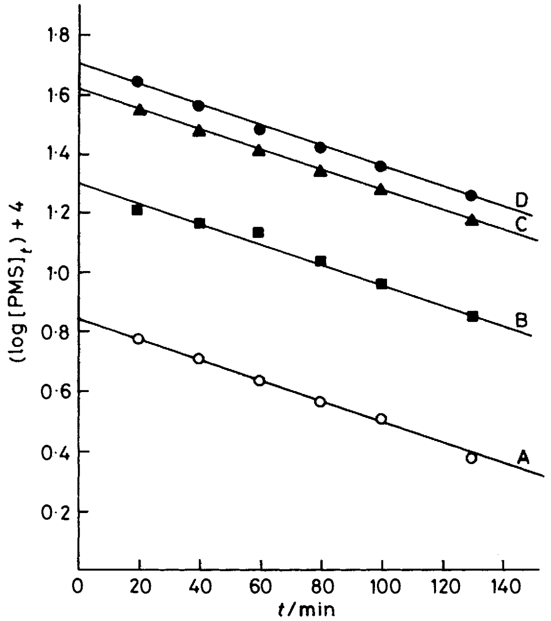


Figure 1. First-order plots in [PMS]: [Ethyl methyl ketone] 0.40 mol dm^{-3}; $[H^+]$ 1.00 mol dm^{-3}; μ 1.20 mol dm^{-3}; T 40 °C. A—D, [PMS] 1, 2, 3, and 4 × 10^{-3} mol dm^{-3}

All the experiments of aliphatic ketones were conducted in aqueous medium whereas, for aromatic ketones, aqueous acetic acid medium (40% acetic acid, v/v) was employed. The acidic medium was provided by 0.20—1.00 mol dm^{-3} H_2SO_4. The condition [substrate] ≫ [PMS] was maintained and the concentration of PMS was varied in the range 1.00—5.00 × 10^{-3} mol dm^{-3} and those of substrates over 1.00—5.00 × 10^{-1} mol dm^{-3}. The effect of $[H^+]$ was studied by varying $[H^+]$ from 0.20 to 1.00 mol dm^{-3} at a constant ionic strength, μ 1.20 mol dm^{-3}. Variation of ionic strength, μ 0.40—1.20 mol dm^{-3}, was carried out to find out the effect of ionic strength on the rate. The effect of dielectric constant was also studied by varying the percentage of acetic acid, in the range 30—70% (v/v).

The kinetics of the reaction was followed by monitoring the disappearance of PMS by iodometry at different intervals. Under the present experimental conditions, no spontaneous self-decomposition as well as carbonyl-assisted decomposition of PMS could be detected.[20a,b,34] The rate constants were obtained using the integral method. By taking a known excess of concentration of PMS over that of ketone and allowing the reaction to go to completion (60 °C), the reaction stoicheiometry was found, [ketone]:[PMS] 1:1. The error limits of the kinetic constants were calculated by the method of least squares. Duplicate experiments were always carried out to check the reproducibility of the results and it was found that the results were reproducible with an error of ±5%.

Product analysis was carried out with [ketone] ≫ [PMS], as in the kinetic runs. The mixture was extracted with ether, after complete disappearance of PMS. Due to the very similar b.p.s of the reactants and of the product, g.l.c. analysis did not give good results. However, the spot test[35] for esters and spectral data (u.v. and i.r.) for esters gave very good results for the formation of the corresponding esters.

Results and Discussion

All the experiments were carried out under pseudo-first-order conditions, [ketone] ≫ [PMS], in the temperature range 30—60 °C at different concentrations of H^+ (0.20—1.00 mol dm^{-3}) but at a constant ionic strength of 1.20 mol dm^{-3}. The oxidations of both aliphatic and aromatic ketones were found to follow total second-order kinetics, first-order in [ketone] and [PMS]. Plots of log $[PMS]_t$ *versus* time were found to be linear showing a first-order dependence on [PMS] (Figure 1). From the slope of the plots, the pseudo-first-order rate constants (k'/

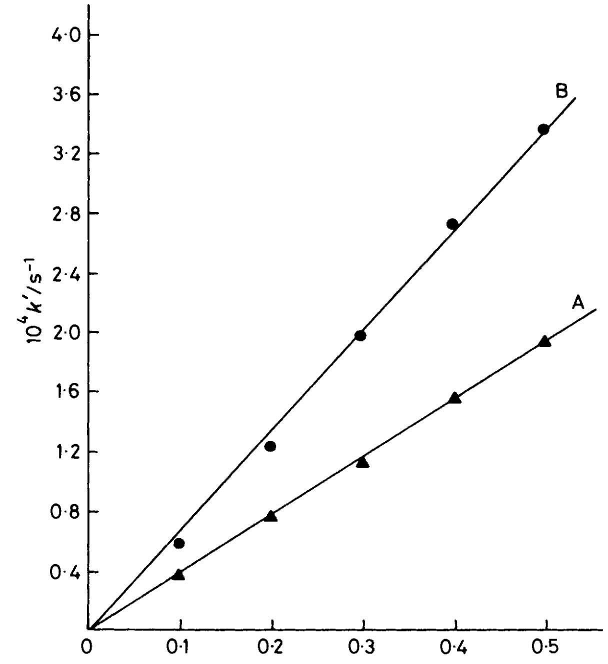


Figure 2. First-order dependence on [ketone]: $[H^+]$ 1.00 mol dm^{-3}; μ 1.20 mol dm^{-3}; T 40 °C. A, Ethyl methyl ketone; B, acetophenone

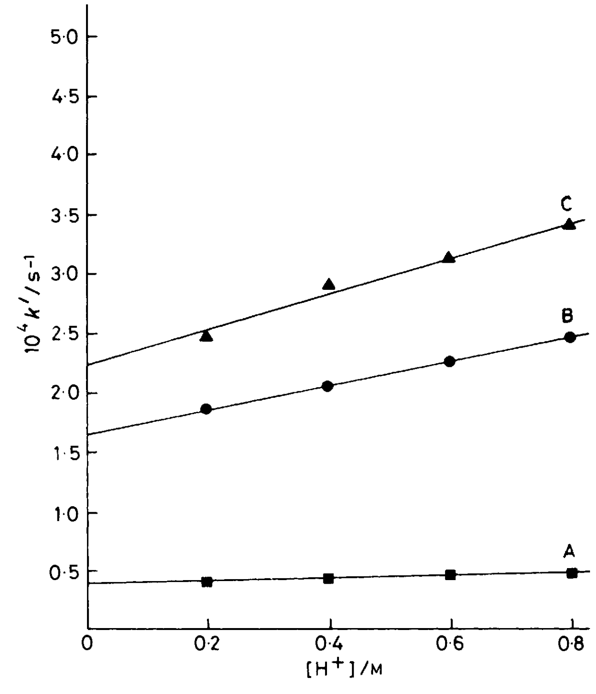


Figure 3. Effect of $[H^+]$ on k_2: [ketone] 4.00 × 10^{-1} mol dm^{-3}; [PMS] 3.00 × 10^{-3} mol dm^{-3}; μ 1.20 mol dm^{-3}; T 50 °C. A, Isobutyl methyl ketone; B, ethyl methyl ketone; C, acetophenone

Table 1. Kinetic and thermodynamic parameters

	Ethyl methyl ketone				Isobutyl methyl ketone			Acetophenone			
	30 °C	40 °C	50 °C	60 °C	40 °C	50 °C	60 °C	30 °C	40 °C	50 °C	60 °C
$10^4\ k_a$/dm^6 mol^{-2} s^{-1}	1.44	1.62	2.50	4.02	0.14	0.52	1.08	1.44	1.94	3.70	7.20
$10^4\ k_b$/dm^3 mol^{-1} s^{-1}	1.18	2.45	4.13	7.58	1.50	1.97	2.75	2.63	3.98	5.56	12.75
$10^4\ k_2$/dm^3 mol^{-1} s^{-1} [a]	2.62	4.07	6.63	11.60	1.64	2.49	3.83	4.07	5.92	9.26	19.95
E_a/kJ mol^{-1}		43.11				35.62			45.96		
$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}		−180.77				−212.46			−167.96		
$\Delta G^{\ddagger}$/kJ mol^{-1}		97.10				99.53			95.93		

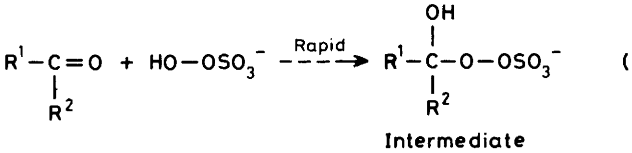
[a] At [H$^+$] 1.00M.

s^{-1}) were evaluated and found to be independent of the initial concentrations of PMS, which further confirms the first-order dependence on [PMS]. The plots of log [PMS]$_t$ *versus* time at different initial concentrations of ketone and at a fixed concentration of PMS were found to be linear for both aliphatic and aromatic ketones. Plots of k' *versus* [ketone] were found to be straight lines passing through the origin (Figure 2), confirming the first-order dependence of rate on [ketone]. The overall second-order rate constants k_2/dm^3 mol^{-1} s^{-1} were evalulated from the slopes of the above plots. This also indicates the absence of self-decomposition[2] and carbonyl-assisted decomposition of PMS.[20a,b,34] The rate of disappearance of PMS was found to be accelerated by increase in [H$^+$] and the plots of k' *versus* [H$^+$] were found to be linear leaving a positive intercept on the ordinate showing the occurrence of acid-dependent and -independent reactions concurrently (Figure 3). The acid-dependent (k_a) and -independent rate constants (k_b) were evaluated respectively from the slopes and intercepts of the plots of k' *versus* [H$^+$]: k_a/dm^6 mol^{-2} s^{-1} = slope/[ketone] and k_b/dm^3 mol^{-1} s^{-1} = intercept/[ketone]. From the second-order rate constants at various temperatures, the values of E_a, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ were calculated using standard equations and are presented in Table 1.

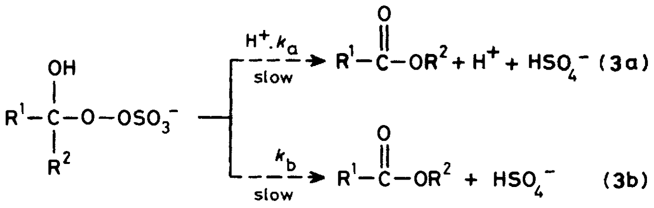
Experiments were carried out to find out whether the reaction involves the formation of free radicals. When a freshly distilled acrylonitrile monomer was added to the deaerated reaction mixture the amount of the polymer formed was found to be equal to that of the polymer formed in the absence of substrate. So it is evident that no polymer was formed by intermediate formed by the reaction of PMS with ketones except by the direct reaction of PMS with the monomer,[16,36] indicating the absence of free radical intermediates in the oxidation of both aliphatic and aromatic ketones. The absence of influence by atmospheric oxygen on the reaction rate together with the total second-order kinetics observed also suggest a non-radical reaction pathway. The effect of ionic strength by added $NaClO_4$ was found to be negligible. The absence of effect of ionic strength on reaction rate predicts[37] that the reaction should involve at least one neutral species, namely the ketone molecule, since the mononegative anion HSO_5^- is known to be the active species of the oxidant at the acidity employed in the investigation.[2]

Most of the features of the Baeyer–Villiger reaction are well understood and it was also known that the Baeyer–Villiger reaction involving various ketones with peroxybenzoic acids is general acid-catalysed[26] and the rate-determining step is either the addition of peracid to carbonyl or migration from the adduct, depending on the substrate.[38] Doering and Speers[27] and Friess[25] showed that the order of increasing migratory aptitudes of alkyl groups in the Baeyer–Villiger reaction is generally methyl < primary < secondary < tertiary. O^{18}-Labelling studies[28] revealed that the carbonyl group of ester formed in the reaction comes from the ketone only.

In the present investigation, from the results obtained, the mechanism of oxidation (2) and (3) may be proposed. The equations for the disappearance of PMS are (4)—(6) where k_2 is



(2)



$$\text{Rate} = -\mathrm{d}[\text{PMS}]/\mathrm{d}t = k_a[\text{PMS}][\text{ketone}][\text{H}^+] + k_b[\text{PMS}][\text{ketone}] \quad (4)$$

$$k' = \text{Rate}/[\text{PMS}] = \{k_a[\text{H}^+] + k_b\}[\text{ketone}] \quad (5)$$

$$k_2 = \text{Rate}/[\text{PMS}][\text{ketone}] = k_a[\text{H}^+] + k_b \quad (6)$$

the overall second-order rate constant and k_a and k_b are the acid-dependent and -independent rate constants, respectively.

The acid catalysis observed in the present investigation may not be due to protonation of the ketones.[21] It is also not possible for peroxomonosulphate to be protonated at the acidity (0.20—1.00 mol dm^{-3}) investigated, since the first pK_a of PMS is equivalent to the first pK_a of H_2SO_4.[2] So it is highly probable that the intermediate formed by the fast addition of PMS to ketone[21] undergoes acid-dependent and -independent processes to form the product. A similar mechanism has been proposed by Ogata *et al.*[39] for the oxidation of acetophenones by peroxomonophosphoric acid, the phosphorus analogue of peroxomonosulphate. In the oxidation of acetophenone by perbenzoic acid, phenyl acetate was identified as the product due to the migration of the phenyl group[26] and with the substituted acetophenone no detectable amount of isomeric methyl ester resulting from methyl group migration was identified.

From the kinetic and thermodynamic parameters (Table 1), it is observed that all the ketones involve a large negative entropy of activation which might be due to severe strain in the formation of activated complex. The magnitude of $\Delta S^{\ddagger}$ observed is similar to those of other similar reactions.[26] In the case of oxidation of ethyl methyl ketone and isobutyl methyl ketone, though the latter involves less energy of activation (35.62 kJ mol^{-1}) than the former (43.11 kJ mol^{-1}) the rate constants are

Table 2. Comparison of the second-order rate constants for the Baeyer–Villiger reactions of acetophenones

Peracid	Temperature T/ °C	Medium	k_2/dm^3 mol^{-1} s^{-1}
HSO_5^-	30	Aqueous acetic acid (40% v/v)	4.07×10^{-4}
H_3PO_5[41]	30	MeCN	2.90×10^{-3}
$PhCO_3H$[26]	23—26	MeCN	1.47×10^{-5}
CF_3CO_3H[29b]	29.8	Ethylene dichloride	2.70×10^{-2}

higher with ethyl methyl ketone due to less negative entropy of activation. An almost constant values of $\Delta G^\ddagger$ for all three ketones investigated may be indicative of the operation of the same mechanism of oxidation, namely a fast nucleophilic attack of peroxomonosulphate on ketone followed by slow reactions (k_a and k_b) to form the products.

Comparison with Similar Peroxides.—Oxidation of ketones by hydrogen peroxide[40] and other organic peroxo acids[24–30] are discussed in terms of nucleophilic reactions. When comparing with peroxodisulphate, $S_2O_8^{2-}$, the reactions take place at a measurable rate only in the presence of a catalyst like Ag^+[41] and the reaction follows a free radical mechanism, unlike that of peroxomonosulphate. In the oxidation of acetophenones by peroxomonophosphate,[39] it was found that the reaction is acid-catalysed and the rate-determining step is the migration of the adduct. A comparative account of peroxoacids reactivity with acetophenone is present in Table 2. It is seen that the reactivity trend is $CF_3CO_3H > H_3PO_5 > HSO_5^- > PhCO_3H$

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References

1 T. S. Price, *J. Chem. Soc.*, 1906, **89**, 54.
2 D. L. Ball and J. O. Edwards, *J. Am. Chem. Soc.*, 1956, **78**, 1125.
3 R. J. Kennedy and A. M. Stock, *J. Org. Chem.*, 1960, **25**, 1901.
4 R. C. Thompson, *Inorg. Chem.*, 1981, **20**, 1005.
5 D. H. Fortnum, C. J. Battaglia, S. R. Cohen, and J. O. Edwards, *J. Am. Chem. Soc.*, 1960, **82**, 778.
6 J. O. Edwards and J. J. Mueller, *Inorg. Chem.*, 1962, **1**, 696.
7 R. W. Johnson and J. O. Edwards, *Inorg. Chem.*, 1966, **5**, 2073.
8 P. Maruthamuthu and P. Neta, *J. Phys. Chem.*, 1977, **81**, 937.
9 P. Maruthamuthu and H. Taniguchi, unpublished results.
10 R. C. Thompson, P. Wieland, and E. H. Appelman, *Inorg. Chem.*, 1979, **18**, 1974.
11 F. C. Chang and K. L. Cheng, *Mikrochim. Acta*, 1979, II, 219.
12 R. C. Thompson, *Inorg. Chem.*, 1982, **21**, 859.
13 A. Nishihara and I. Kubota, *J. Org. Chem.*, 1968, **33**, 2525.
14 R. Somuthevan, R. Renganathan, and P. Maruthamuthu, *Inorg. Chim. Acta Lett.*, 1980, **45**, 165.
15 V. Meenakshi, M. Phil Dissertation, University of Madras, 1983.
16 T. Pandurengan and P. Maruthamuthu, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 3551.
17 T. S. Jani Bai, M. Phil Dissertation, University of Madras, 1983.
18 A. A. Jameel, M. Phil Dissertation, University of Madras, 1983.
19 P. Kanagaraj and P. Maruthamuthu, *Int. J. Chem. Kinet.*, 1983, **15**, 1301.
20 (*a*) R. E. Montgomery, *J. Am. Chem. Soc.*, 1974, **96**, 7820; (*b*) U.S.P. 3,822,114/1974.
21 R. Curci, M. Fiorentino, L. Troisi, J. O. Edwards, and R. H. Pater, *J. Org. Chem.*, 1980, **45**, 4758.
22 J. March, 'Advanced Organic Chemistry: Reactions, Mechanism and Structure,' McGraw-Hill, New York, 1968, p. 822.
23 A. von Baeyer and V. Villiger, *Ber.*, 1899, **32**, 3625.
24 S. L. Friess, *J. Am. Chem. Soc.*, 1949, **71**, 14.
25 S. L. Friess and N. Farnham, *J. Am. Chem. Soc.*, 1950, **72**, 5518.
26 S. L. Friess and A. H. Soloway, *J. Am. Chem. Soc.*, 1951, **73**, 3968.
27 W. von E. Doering and L. Speers, *J. Am. Chem. Soc.*, 1950, **72**, 5515.
28 W. von E. Doering and E. Dorfman, *J. Am. Chem. Soc.*, 1953, **75**, 5595.
29 M. F. Hawthrone, W. D. Emmons, and K. S. McCallum, *J. Am. Chem. Soc.*, 1958, **80**, (*a*) 6393; (*b*) 6398.
30 W. V. Steele and E. H. Appelman, *J. Chem. Thermodyn.*, 1982, **14**, 337.
31 (*a*) R. Renganathan, Ph.D.Thesis, University of Madras, 1984; (*b*) R. Renganathan and P. Maruthamuthu, *J. Chem. Soc., Perkin Trans. 2*, 1986, 285.
32 Technical data on 'Oxone', du Pont de Nemours and Co., U.S.A., 1979.
33 K. J. P. Orton and A. E. Bradfield, *J. Chem. Soc.*, 1927, 983.
34 S. Ch. Dharma Rao, A. K. Panda, and S. N. Mahapatra, *J. Chem. Soc., Perkin Trans. 2*, 1983, 769.
35 H. T. Clarke and B. Haynes, 'A Hand Book of Organic Analysis, Qualitative and Quantitative,' Edward Arnold, London, 5th. edn., p. 55.
36 G. Manivannan and P. Maruthamuthu, to be published.
37 K. J. Laidler, 'Chemical Kinetics,' Tata-McGraw-Hill, New Delhi, India, 1983, p. 229.
38 Y. Ogata and Y. Sawaki, *J. Org. Chem.*, 1972, **37**, 2953.
39 Y. Ogata, K. Tomizawa, and T. Ikeda, *J. Org. Chem.*, 1978, **43**, 2417.
40 G. Mehta and N. P. Pandey, *Synthesis*, 1975, 404.
41 L. R. Subbaraman and M. Santappa, *Z. Phys. Chem. (Frankfurt)*, 1966, **48**, 172.

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