Kinetics and Mechanism of Oxidation of Aromatic Aldehydes by Peroxomonosulphate

Rajalingam Renganathan and Pichai Maruthamuthu *
Department of Energy, University of Madras, A.C. College Campus, Madras 600 025, India

The kinetics of oxidation of benzaldehydes by peroxomonosulphate (PMS) have been measured in aqueous acetic acid medium (30—70% v/v) in the presence of $HClO_4$ (0.10—1.00 mol dm^{-3}) at constant ionic strength (1.20 mol dm^{-3}) over the temperature range 10—60 °C. The reactions have been found to obey the rate law (i) for the disappearance of PMS, indicating the concurrent occurrence of both the

$$\text{Rate} = \{k_a[H^+] + k_0\}[\text{PMS}][\text{aldehyde}] \quad \text{(i)}$$

acid-dependent and acid-independent reaction paths. Oxidation of substituted benzaldehydes afforded phenols by aryl migration and benzoic acids by hydride migration. The characteristic ρ values, +1.81 for hydride and −1.70 for aryl migration, are discussed in terms of the mechanism of oxidation involving the fast nucleophilic addition of peroxide to the carbonyl group followed by the rate-determining acid-catalysed and uncatalysed reaction paths, the other experimental observations also being taken into account. The product distribution and the difference in the reactivity of peroxomonosulphate observed in the present investigation from those of the corresponding reactions of peroxomonophosphate are attributed to the better oxidising power of, and the better leaving group (SO_4^{2-} or HSO_4^-) from, peroxomonosulphate. Thermodynamic parameters have been evaluated to substantiate the mechanism proposed.

Kinetic investigations on the oxidation of organic and inorganic substrates with the well known oxidant, peroxodisulphate (PDS), have been carried out by many research workers.[1–3] Recently the corresponding monoperoxo compound, namely peroxomonosulphate (PMS), has attracted the attention of many research workers. Peroxomonosulphate and peroxodisulphate bear relation in their structures as the derivatives of H_2O_2 replacing one or both the hydrogen atoms in H_2O_2 by an SO_3 group. Simple metal-ion-catalysed[4a] as well as the dual system Ag^+–$S_2O_8^{2-}$-catalysed[4b] and uncatalysed[5] thermal decompositions of peroxomonosulphate (PMS) and oxidation of chloride,[6] bromide, iodide,[7] nitrite,[8] chlorite,[9] and hypophosphite[10] ions have been carried out. Recently, radiolytic chain decomposition,[11] *in situ* photolysis-e.s.r.,[12] flash photolysis[13] of PMS, and photochemical chain decomposition of peroxomonosulphate in the presence and absence of propan-2-ol[14] have been carried out. Oxidation of organic substrates like aldehydes,[15] dimethyl sulphoxide,[16] pyridine,[17] *o*-benzoquinone,[18] glycine,[19] cyclopentanone,[20] cyclohexanone,[21] and anilines[22] by peroxomonosulphate have been carried out. Peroxomonosulphate is found to undergo reactions by different types of mechanisms (free radical, nucleophilic, or electrophilic) in the investigations mentioned above. It has been also observed that peroxomonosulphate is a better oxidant than peroxodisulphate in the oxidation of halide ions.[6] The present study involves the oxidation of benzaldehyde and substituted benzaldehyde by peroxomonosulphate. In this study, it is proposed to find out: (i) whether the reactions follow free-radical pathways or polar mechanisms, (ii) the effect of $[H^+]$ since the reactions of peroxides are prone to acid catalysis, (iii) the effect of substituents on the reactivities of benzaldehydes and product distribution, (iv) the mechanistic aspects resulting from the kinetic and thermodynamic data, and (v) the relationship of the kinetic parameters and the reactivity with the corresponding reactions of similar peroxides, peroxodisulphate, $S_2O_8^{2-}$ and peroxomonophosphate, $H_2PO_5^-$.

Experimental

All the chemicals used were of AnalaR grade. Potassium peroxomonosulphate was a gift from du Pont de Nemours under the trade name oxone.[23] 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 purify the compound further because of previous unsuccessful attempts.[11] From the methods of preparation of this compound, it is assumed that that $KHSO_4$ or K_2SO_4 or both might account for the 4% difference between the formula and analysis results. Benzaldehyde (B.D.H. AnalaR) was used after distillation, b.p. 179—179.5 °C. All the other aromatic aldehydes, *o*-chlorobenzaldehyde, *o*-methoxybenzaldehyde, *o*-nitrobenzaldehyde, *m*-bromobenzaldehyde, *m*-chlorobenzaldehyde, *m*-methoxybenzaldehyde, *m*-nitrobenzaldehyde, *p*-bromobenzaldehyde, *p*-methoxybenzaldehyde, *p*-nitrobenzaldehyde, and *p*-tolualdehyde were the purest samples available from Fluka and were used as such. Acetic acid used as solvent was purified (to 99.9%) before use. Other chemicals were analytical grade samples from B.D.H., and sodium perchlorate was from E. Merck.

Experiments were carried out in aqueous acetic acid medium (30—70% v/v) at a constant ionic strength of 1.20 mol dm^{-3} maintained by the addition of $NaClO_4$. The effect of $[H^+]$ on the rate was studied by carrying out the kinetic runs with $[H^+]$ 0.10—1.00 mol dm^{-3}. Under the present experimental conditions, no spontaneous self-decomposition[4a] as well as carbonyl-assisted decomposition[17,24,25] of the oxidant could be detected. The kinetics of the reaction was followed by monitoring the disappearance of peroxomonosulphate by iodometry at different time intervals. The rate constants were obtained by integral methods. The stoicheiometry of the reaction was established by estimating unchanged PMS by iodometry and the aldehydes by the 2,4-dinitrophenylhydrazone method.[26] Product analysis was carried out under the condition [aldehyde] ≫ [PMS], as in the kinetic runs. After the complete

Table 1. First-order dependence on [PMS]

[Benzaldehyde] 3.00 × 10^{-2} mol dm^{-3}, [H$^+$] 0.26 mol dm^{-3}, acetic acid 40% (v/v), μ 1.20 mol dm^{-3}, T 40 °C

10^3[PMS]/mol dm^{-3}	1.10	1.50	2.10	2.60	3.10
10^4 k'/s^{-1}	1.33	1.33	1.32	1.30	1.32

[*o*-Chlorobenzaldehyde] 3.00 × 10^{-2} mol dm^{-3}, [H$^+$] 0.40 mol dm^{-3}, acetic acid 60% (v/v), μ 1.20 mol dm^{-3}, T 40 °C

10^3[PMS]/mol dm^{-3}	1.60	2.10	2.80	3.10	3.30
10^4 k'/s^{-1}	1.44	1.44	1.43	1.43	1.45

[*m*-Nitrobenzaldehyde] 3.00 × 10^{-2} mol dm^{-3}, [H$^+$] 0.40 mol dm^{-3}, acetic acid 40% (v/v), μ 1.20 mol dm^{-3}, T 40 °C

10^3[PMS]/mol dm^3	1.40	1.80	2.00	2.50	2.80
10^4 k'/s^{-1}	5.42	5.44	5.45	5.40	5.46

[*p*-Bromobenzaldehyde] 3.00 × 10^{-2} mol dm^{-3}, [H$^+$] 0.40 mol dm^{-3}, acetic acid 40% (v/v), μ 1.20 mol dm^{-3}, T 40 °C

10^3[PMS]/mol dm^{-3}	1.90	2.40	3.10	3.30	3.70
10^4 k'/s^{-1}	3.05	3.05	3.04	3.06	3.07

Table 2. First-order dependence on [aldehyde]

Benzaldehyde

[PMS] 1.10 × 10^{-3} mol dm^{-3}, [H$^+$] 0.26 mol dm^{-3}, acetic acid 40% (v/v), μ 1.20 mol dm^{-3}, T 40 °C

10^2[Benzaldehyde]/mol dm^{-3}	1.00	2.00	3.00	4.00	5.00
10^4 k'/s^{-1}	0.50	0.96	1.37	1.86	2.24

o-Chlorobenzaldehyde

[PMS] 1.00 × 10^{-3} mol dm^{-3}, [H$^+$] 0.40 mol dm^{-3}, acetic acid 60% (v/v), μ 1.20 mol dm^{-3}, T 50 °C

10^2[*o*-Chlorobenzaldehyde]/mol dm^{-3}	1.00	2.00	3.00	4.00
10^4 k'/s^{-1}	0.46	0.90	1.39	1.84

p-Tolualdehyde

[PMS] 1.10 × 10^{-3} mol dm^{-3}, [H$^+$] 0.26 mol dm^{-3}, acetic acid 40% (v/v), μ 1.20 mol dm^{-3}, T 40 °C

10^2[*p*-Tolualdehyde]/mol dm^{-3}	1.00	2.00	3.00	4.00
10^5 k'/s^{-1}	4.50	9.20	14.00	18.50

p-Bromobenzaldehyde

[PMS] 1.10 × 10^{-3} mol dm^{-3}, [H$^+$] 0.40 mol dm^{-3}, acetic acid 40% (v/v), μ 1.20 mol dm^{-3}, T 40 °C

10^2[*p*-Bromobenzaldehye]/mol dm^{-3}	1.00	2.00	3.00	4.00	5.00
10^4 k'/s^{-1}	1.08	1.95	3.00	3.95	4.91

disappearance of PMS, the mixture was extracted with ether. The ether extract was dried with (Na_2SO_4) and evaporated and the residue containing the product and unchanged substrate was then analysed by g.c. after converting the acid products into methyl ester by reaction with diazomethane, and phenols into methyl ether by reaction with dimethyl sulphate. The g.c. measurements were carried out with Varian model 3700 gas chromatograph attached to a Varian CDS 401 microprocessor. Identification of the products was made by comparison of retention time data of authentic samples. Duplicate experiments were always carried out to estimate the reproducibility of the results (±5%). The least-squares method was employed to estimate the uncertainties in the values of the kinetic and thermodynamic parameters.

Results and Discussion

All the experiments were carried out under pseudo-first-order conditions, [aldehyde] $\gg$ [PMS]. Most of the experiments were carried out with 40% (v/v) acetic acid. The kinetics of the reactions was studied with [PMS] 1.10—3.70 × 10^{-3} mol dm^{-3}, [aldehyde] 1.00—5.00 × 10^{-2} mol dm^{-3}, and [H$^+$] 0.10—1.00 mol dm^{-3}. Plots of log [PMS] *versus* time were found to be linear indicating a first-order dependence on [PMS]. The pseudo-first-order rate constants, k'/s^{-1}, calculated from the slopes of the above plots were found to be independent (Table 1) of the initial concentrations of PMS, further confirming the first-order dependence of the rate on [PMS] for all the aldehydes investigated. Variation of [aldehyde] at a fixed concentration of PMS was found to enhance the rate of disappearance of PMS and the corresponding plots of log [PMS] *versus* time were found to be linear with increasing values of k' (k'/s^{-1} = slope × 2.303/60) with increasing [aldehyde] (Table 2). The values of k', when plotted against [aldehyde], gave straight lines (Figure 1) passing through the origin, confirming the first-order dependence with respect to [aldehyde] and also indicating the absence of self-decomposition[4a] as well as the carbonyl-assisted decomposition[22,27,28] of peroxomonosulphate. The overall second-order rate constants, k_2/dm^3 mol^{-1} s^{-1}, were calculated from the slopes of the above plots. Increase of [H$^+$] (0.10—1.00 mol dm^{-3}) at constant [PMS], [aldehyde], and ionic strength is found to increase the reaction rate. Plots of k' *versus* [H$^+$] (Figure 2) were found to be linear with an intercept on the ordinate, indicating the concurrent occurrence of both acid-dependent and -independent reactions. This is found to be true for all the aldehydes investigated. The

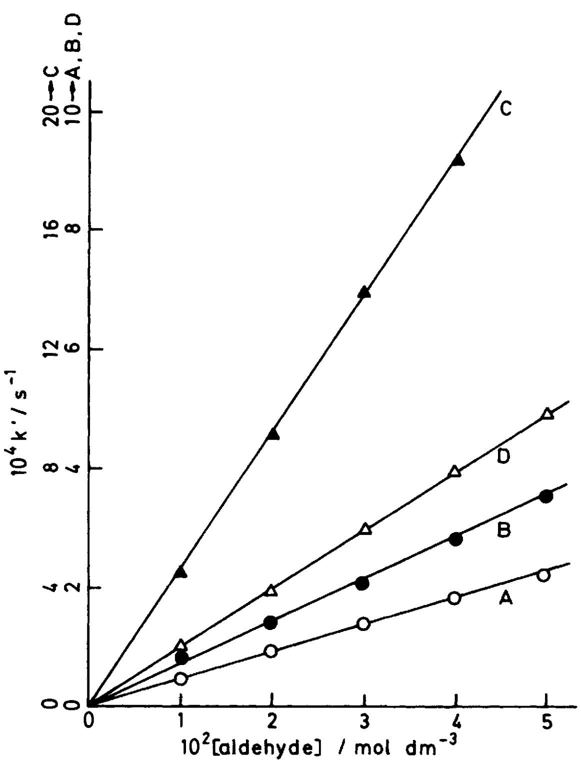


Figure 1. k' *versus* [aldehyde], A, [PMS] 1.10 × 10^{-3} mol dm^{-3}, [benzaldehyde] 1.00—5.00 × 10^{-2} mol dm^{-3}, [H$^+$] 0.26 mol dm^{-3}, acetic acid 40% (v/v), μ 1.20 mol dm^{-3}, T 40 °C; B, [PMS] 1.00 × 10^{-3} mol dm^{-3}, [*o*-chlorobenzaldehyde] 1.00—5.00 × 10^{-3} mol dm^{-3}, [H$^+$] 0.40 mol dm^{-3}, acetic acid 60% (v/v), μ 1.20 mol dm^{-3}, T 50 °C; C, [PMS] 1.10 × 10^{-3} mol dm^{-3}, [*p*-tolualdehyde] 1.00—4.00 × 10^{-2} mol dm^{-3}, [H$^+$] 0.26 mol dm^{-3}, acetic acid 40% (v/v), μ 1.20 mol dm^{-3}, T 40 °C; D, [PMS] 1.10 × 10^{-3} mol dm^{-3}, [*p*-bromobenzaldehyde] 1.00—5.00 × 10^{-2} mol dm^{-3}, [H$^+$] 0.40 mol dm^{-3}, acetic acid 40% (v/v), μ 1.20 mol dm^{-3}, T 40 °C

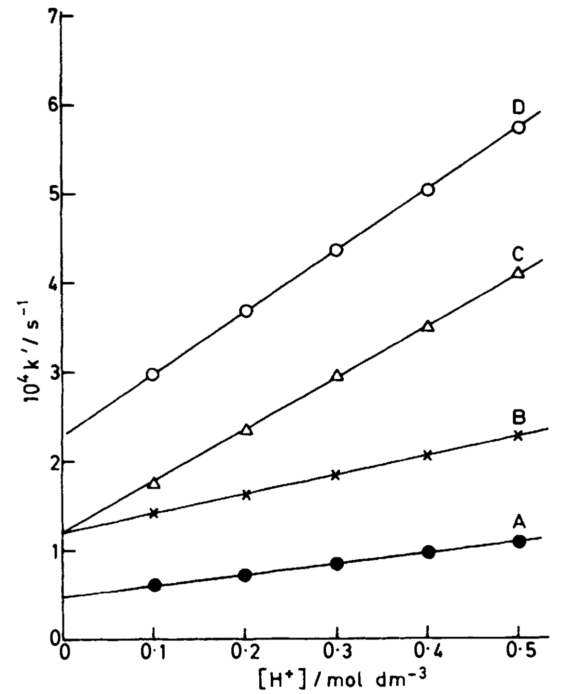
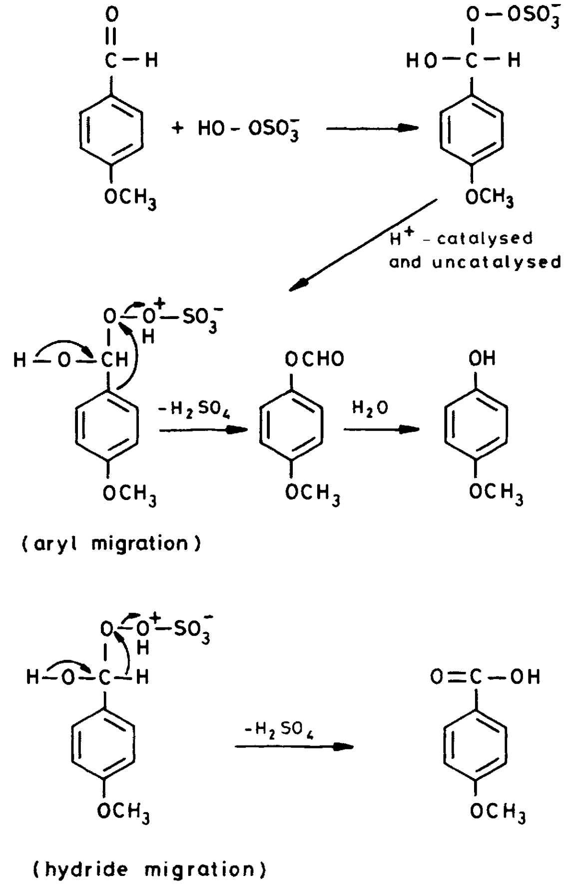


Figure 2. k' *versus* $[H^+]$. A, [PMS] 1.00×10^{-3} mol dm^{-3}, [benzaldehyde] 3.00×10^{-2} mol dm^{-3}, $[H^+]$ 0.20—1.00 mol dm^{-3}, acetic acid 40% (v/v), μ 1.20 mol dm^{-3}, T 40 °C; B, [PMS] 2.00×10^{-3} mol dm^{-3}, [*o*-chlorobenzaldehyde] 2.00×10^{-2} mol dm^{-3}, $[H^+]$ 0.10—0.50 mol dm^{-3}, acetic acid 60% (v/v), μ 1.20 mol dm^{-3}, T 40 °C; C, [PMS] 2.00×10^{-3} mol dm^{-3}, [*m*-nitrobenzaldehyde] 2.00×10^{-2} mol dm^{-3}, $[H^+]$ 0.10—0.50 mol dm^{-3}, acetic acid 40% (v/v), μ 1.20 mol dm^{-3}, T 40 °C; D, [PMS] 5.10×10^{-3} mol dm^{-3}, [*p*-bromobenzaldehyde] 5.00×10^{-2} mol dm^{-3}, $[H^+]$ 0.10—0.50 mol dm^{-3}, acetic acid 40% (v/v), μ 1.20 mol dm^{-3}, T 40 °C



Scheme.

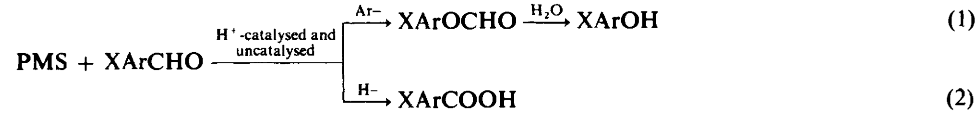
acid-dependent (k_a) and -independent (k_0) rate constants were obtained respectively from the slope and intercept of the plots of k' *versus* $[H^+]$.

For all the substrates investigated, the rates were found to decrease with increase in the percentage of acetic acid, *i.e.*, with decreasing dielectric constant of the solvent mixture, showing that there is charge development in the transition state[29] involving a more polar activated complex than the reactants, a neutral molecule (aldehyde), and negative ion (HSO_5^-).

The presence or absence of atmospheric oxygen was found to have no effect on the reaction rate. The effect of ionic strength by added $NaClO_4$ was found to be negligible, indicating the involvement of one neutral species, namely the aldehyde molecule, and HSO_5^- which is found to be the active species of the oxidant, PMS, under the present experimental conditions.

It is reported that benzaldehyde and most of its substituted derivatives are not hydrated to any appreciable extent.[30,31] Moreover, no reaction is known in which nucleophilic attack on tetrahedral carbon as in an aldehyde hydrate is faster than that on the free aldehyde[27] ArCHO. So it is fair to assume that the free HC=O group of the aldehyde acts as the active species of the substrate as in the case of oxidation of aromatic aldehydes by peroxomonophosphate.[27] The acid dependence observed is attributed to the acid-catalysed decomposition of the adduct formed by the fast addition of peroxomonosulphate to the aldehydes. Two kinds of products are found to be formed depending upon the migration of hydride and/or aryl group. Taking *p*-methoxybenzaldehyde as an example, the products formation by aryl and hydride migration may be represented by the Scheme. In the case of benzaldehyde oxidation, only benzoic acid was identified which is due to hydride migration and there was no phenol formed.

In general, product formation may be represented by reactions (1) and (2) where Ar– and H– represent aryl and hydride migration respectively.



$$\text{PMS} + \text{XArCHO} \xrightarrow[\text{uncatalysed}]{\text{H}^+\text{-catalysed and}} \begin{cases} \xrightarrow{\text{Ar}-} \text{XArOCHO} \xrightarrow{H_2O} \text{XArOH} & (1) \\ \xrightarrow{\text{H}-} \text{XArCOOH} & (2) \end{cases}$$

From Table 3, it is clear that electron-withdrawing substituents favour the formation of the corresponding acid and electron-donating substituents favour the formation of the corresponding phenol. Similar observation has been made by Ogata *et al.*[27] in the oxidation of benzaldehydes by peroxomonophosphate.

The general rate equations for the oxidation of aromatic aldehydes are (3)—(5) where k_a and k_0 are acid-dependent and -independent rate constants respectively.

Comparing the overall rate constants (Table 3) at 30 °C, it is

Table 3. Substituent effects. Kinetic constants and the estimated product distribution for the oxidation of benzaldehydes

$[H^+]$ 0.40 mol dm^{-3}, T 30 °C

Substituent	$10^3\ k_2$/dm^3 mol^{-1} s^{-1}	$10^3\ k_H$/dm^3 mol^{-1} s^{-1}	$10^3\ k_{Ar}$/dm^3 mol^{-1} s^{-1}	% of benzoic acid formed by hydride migration	% of phenol formed by aryl migration
H	3.03	3.03	0	100	0
m-Br	5.96	4.77	1.19	80	20
p-Br	6.21	5.90	0.31	95	5
o-Cl	2.80	1.68	1.12	60	40
m-Cl	4.27	3.63	0.64	85	15
o-NO_2	3.27	2.29	0.98	70	30
m-NO_2	11.20	10.64	0.56	95	5
p-NO_2	16.30	16.30	0	100	0
o-OCH_3	44.70	15.65	227.50	35	65
m-OCH_3	7.13	2.14	4.99	30	70
p-OCH_3	22.40	3.36	19.04	15	85
p-CH_3	3.50	0.35	3.15	10	90

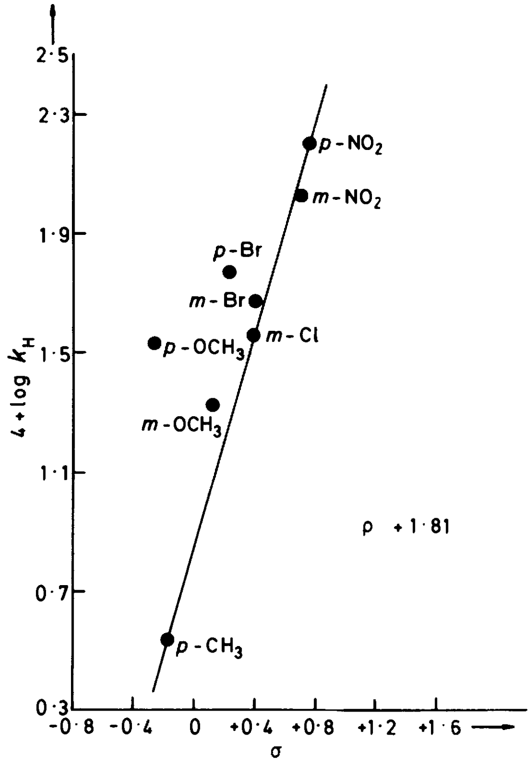


Figure 3. Hammett plot for hydride migration. Evaluation of ρ (log k_H *versus* σ). $[H^+]$ 0.40 mol dm^{-3}, T 30 °C

$$-d[PMS]/dt = \text{rate} =$$

$$k_a[PMS][\text{aldehyde}][H^+] + k_0[PMS][\text{aldehyde}] \quad (3)$$

$$\text{rate}/[PMS] = k' = [\text{aldehyde}]\{k_a[H^+] + k_0\} \quad (4)$$

$$k_2/\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1} = k'/[\text{aldehyde}] = k_a[H^+] + k_0 \quad (5)$$

found that the rate constant for *o*-methoxybenzaldehyde is at a maximum and is twice as high as that for *p*-methoxybenzaldehyde revealing the relative unimportance of steric effects. The electron-withdrawing substituents *o*-Cl and *o*-NO_2 exhibit lower reactivity than those at the *meta*- and *para*-positions. Generally, the electron-withdrawing groups are found

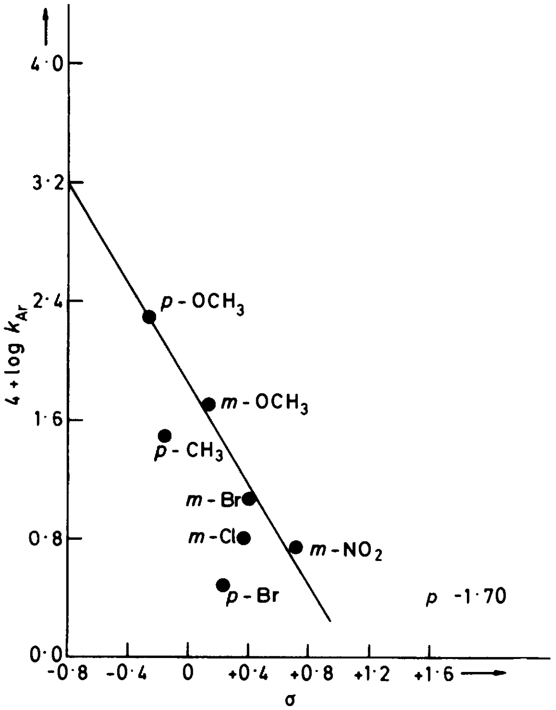


Figure 4. Hammett plot for aryl migration. Evaluation of ρ (log k_{Ar} *versus* σ). $[H^+]$ 0.40 mol dm^{-3}, T 30 °C

Table 4. Evaluation of ρ. Hammett plot

$[H^+]$ 0.40 mol dm^{-3}, T 30 °C

Substituent	σ	4 + log k_H	4 + log k_{Ar}
m-Br	+0.391	1.6785	1.0755
p-Br	+0.232	1.7709	0.4914
m-Cl	+0.373	1.5599	0.8062
m-NO_2	+0.710	2.0270	0.7482
p-NO_2	+0.778	2.2122	0
m-OCH_3	+0.115	1.3304	1.6981
p-OCH_3	−0.268	1.5263	2.2797
p-CH_3	−0.170	0.5441	1.4983
ρ		+1.81	−1.70

Table 5. Activation parameters for the overall rate constants (k_2)

Substrate	E_a/kJ mol^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}	$\Delta G^{\ddagger}$/kJ mol^{-1}
Benzaldehyde	33.97 ± 0.02	31.38	−189.91	90.83
o-Chlorobenzaldehyde	41.21 ± 0.006	38.62	−166.65	90.75
o-Methoxybenzaldehyde	32.38 ± 0.07	29.79	−173.38	84.06
o-Nitrobenzaldehyde	33.30 ± 0.03	30.71	−191.21	90.54
m-Bromobenzaldehyde	43.60 ± 0.02	41.00	−152.34	88.70
m-Chlorobenzaldehyde	32.72 ± 0.05	30.12	−191.21	89.96
m-Methoxybenzaldehyde	26.36 ± 0.01	23.77	−207.65	88.74
p-Bromobenzaldehyde	34.06 ± 0.03	31.46	−183.22	88.83
p-Methoxybenzaldehyde	38.91 ± 0.01	36.32	−156.90	85.44
p-Nitrobenzaldehyde	34.89 ± 0.01	32.30	−172.84	86.40
p-Tolualdehyde	24.52 ± 0.05	21.91	−220.25	90.88

to favour hydride migration and electron-donating groups favour aryl migration. Among the electron-donating groups, CH_3 and OCH_3, the reactivity trend is in the order p-CH_3 < m-OCH_3 < p-OCH_3 < o-OCH_3. Among the electron-withdrawing substituents, the reactivity trend observed is p-NO_2 > m-NO_2 > p-Br > m-Br > m-Cl > o-NO_2 > o-Cl. Multiplying the values of k_2 (overall second-order rate constant) with the product selectivity, the rate constants for hydride and aryl migrations are calculated.[27] From the plot of log K_H *versus* σ (Figure 3), the ρ value (Table 4) for hydride migration is calculated and found to be in good agreement with the ρ (+1.74) observed for the corresponding reaction of peroxomonophosphate (PMP) with benzaldehydes.[27] However, for aryl migration, from the plot of log k_{Ar} *versus* σ (Figure 4), the observed value of ρ in the present investigation (Table 4) is less negative than that observed in the PMP oxidation (−2.88).[27] This discrepancy may be due to the difference in the reaction conditions, the PMP reactions being carried out at pH 1.3 and above whereas the present work involves $[H^+]$ 0.40 mol dm^{-3}. Similar values of ρ, as exhibited in the present investigation, have been observed in Baeyer–Villiger oxidations involving the slow and rate-determining migration step.[28,32] It is also known that the rate of the Baeyer–Villiger reaction changes with substrate and pH for various peroxide reactions.[27] The $\Delta S^{\ddagger}$ values (Table 5) are found to be highly negative indicating the formation of a severely structured transition state. The values of $\Delta S^{\ddagger}$ observed in this investigation are very similar to the values reported by Panigrahi and Panda in the reactions of *para*-substituted benzaldehydes with peroxomonophosphate[33] at 0.5 mol dm^{-3} H^+. The similar values of $\Delta G^{\ddagger}$ (Table 5) observed in the present investigation may indicate that the mechanism operative is similar for all the reactions.

Comparison with Similar Peroxides.—Peroxomonosulphate is found to undergo nucleophilic reactions with aromatic aldehyde, whereas the available literature on peroxodisulphate (PDS)[34] oxidation of benzaldehyde shows that the reaction follows a free-radical mechanism involving $SO_4^{\bullet -}$ as the reaction intermediate.

Comparing the results of oxidation of benzaldehydes by peroxomonophosphate[27,33] in acidic medium with those of the present investigation, it is found that these two oxidants behave similarly: (i) the reactions exhibit non-radical overall second-order kinetics, (ii) the mechanisms involve fast addition of the peroxide with aldehydes followed by the rate-determining hydride or aryl migration, and (iii) they exhibit product selectivites and correlation of substituent constants (σ) with the rate constants of hydride and aryl migration steps. The behaviour of peroxomonosulphate is also similar to the other organic peroxides[35,36] undergoing nucleophilic reactions with benzaldehydes. However, the product distribution and reactivity differ due to the better oxidising power of, and the better leaving group (SO_4^{2-} or HSO_4^-) from, peroxomonosulphate.

References

1 W. K. Wilmarth and A. Haim, in 'Peroxide Reaction Mechanisms,' ed. J. O. Edwards, Wiley-Interscience, New York, 1962, p. 175.
2 D. A. House, *Chem. Rev.*, 1962, **62**, 185.
3 E. J. Behrman and J. E. McIsaac, Jr., in 'Mechanism of Reactions of Sulphur Compounds,' ed. N. Kharasch, Interscience, Los Angeles, 1968, 2nd edn., p. 193.
4 (*a*) D. L. Ball and J. O. Edwards, *J. Am. Chem. Soc.*, 1956, **78**, 1125; (*b*) R. C. Thompson, *Inorg. Chem.*, 1981, **20**, 1005.
5 D. L. Ball and J. O. Edwards, *J. Phys. Chem.*, 1958, **62**, 343.
6 D. H. Fortnum, C. J. Battaglia, S. R. Cohen, and J. O. Edwards, *J. Am. Chem. Soc.*, 1960, **82**, 778.
7 F. Secco and M. Venturini, *J. Chem. Soc., Dalton Trans.*, 1976, 1410.
8 J. O. Edwards and J. J. Mueller, *Inorg. Chem.*, 1962, **1**, 696.
9 R. W. Johnson and J. O. Edwards, *Inorg. Chem.*, 1966, **5**, 2073.
10 V. Meenakshi, M.Phil. Dissertation, University of Madras, 1983.
11 P. Maruthamuthu and P. Neta, *J. Phys. Chem.*, 1977, **81**, 937.
12 P. Maruthamuthu and H. Taniguchi, unpublished results.
13 V. D. McGinniss and A. F. Kah, *J. Coat. Technol.*, 1979, **51**, 81.
14 P. Kanagaraj and P. Maruthamuthu, *Int. J. Chem. Kinet.*, 1983, **15**, 1301.
15 A. Nishihara and I. Kubota, *J. Org. Chem.*, 1968, **33**, 2525.
16 T. Pandurengan and P. Maruthamuthu, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 3551.
17 A. R. Gallopo and J. O. Edwards, *J. Org. Chem.*, 1981, **46**, 1684.
18 W. Ando, H. Miyaziki, and T. Akasaka, *J. Chem. Soc., Chem. Commun.*, 1983, 518.
19 T. S. Jani Bai, M.Phil. Dissertation, University of Madras, 1983.
20 T. Narpasalai, M.Phil. Dissertation, University of Madras, 1983.
21 P. Dharmalingam and P. Maruthamuthu, to be published.
22 A. A. Jameel, M.Phil. Dissertation, University of Madras, 1983.
23 Technical data on Oxone, E. I. du Pont de Nemours & Co., 1979.
24 R. E. Montgomery, *J. Am. Chem. Soc.*, 1974, **96**, 7820.
25 S.Ch. Dharma Rao, A. K. Panda, and S. N. Mahapatro, *J. Chem. Soc., Perkin Trans. 2*, 1983, 769.
26 'A Text-book of Practical Organic Chemistry,' ed. A. I. Vogel, Longman, London, 1968, p. 720.
27 Y. Ogata, Y. Sawaki, and Y. Tsukamoto, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 2061.
28 M. F. Hawthorne and W. D. Emmons, *J. Am. Chem. Soc.*, 1958, **80**, 6393.
29 K. J. Laidler, 'Chemical Kinetics,' Tata–McGraw-Hill, New Delhi, 1965, p. 228.
30 W. J. Bover and P. Zuman, *J. Chem. Soc., Perkin Trans. 2*, 1973, 786.
31 J. M. Sayer, *J. Org. Chem.*, 1975, **40**, 2545.
32 B. W. Palmer and A. Fry, *J. Am. Chem. Soc.*, 1970, **92**, 2580.
33 G. P. Panigrahi and R. Panda, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 3084.
34 S. P. Srivastava, G. L. Maheshwari, and S. K. Singhal, *Indian J. Chem.*, 1974, **12**, 72.
35 Y. Ogata and Y. Sawaki, *J. Org. Chem.*, 1969, **34**, 3985.
36 Y. Ogata and Y. Sawaki, *J. Am. Chem. Soc.*, 1972, **94**, 4189.

Received 20*th May* 1985; *Paper* 5/848