

Mechanism of the Oxidation of Alkyl Aryl Sulphides by Peroxodiphosphate

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The kinetics of oxidation of alkyl aryl sulphides by peroxodiphosphate ion were investigated in 50% (v/v) aqueous acetic acid. At constant $[H^+]$ and ionic strength, the reaction is second-order, first-order in sulphide and in peroxodiphosphate. An analysis of the dependence of the rate of oxidation of methyl phenyl sulphide on $[H^+]$ shows that $H_3P_2O_8^-$ is the active species involved in the oxidation process. The rate of the reaction is influenced by changing the ionic strength. Acrylonitrile has no effect on the rate of oxidation. In substituted phenyl methyl sulphides, the rate of the reaction is accelerated by electron-donating substituents and retarded by electron-withdrawing substituents, indicating rate-determining nucleophilic displacement by the sulphide sulphur on the peroxide oxygen. The ρ value obtained at 40 °C ($\rho -0.619$, $r 0.994$, $s 0.03$, confidence limit on $\rho \pm 0.04$) by correlation analysis of the rate constants with σ^+ and σ^- constants, reveals the existence of an excellent linear free-energy relationship. The activation parameters and the isokinetic temperature have been determined. Studies with different alkyl phenyl sulphides (C_6H_5SR ; $R = Me, Et, Pr^i, Pr^t, \text{ or } Bu^t$) indicate that the reaction rate is retarded by bulky R groups. On the basis of the kinetic studies, a suitable mechanism has been proposed.

SINCE the initial preparation of peroxodiphosphate by Schmidlin and Massini¹ in 1910, the kinetics of its oxidation of both inorganic and organic substrates has received relatively little attention in comparison with the kinetics of oxidation by peroxodisulphate.²⁻⁴ Interest in its use as an oxidant in kinetics is of recent origin and a few studies have been reported by Edwards,⁵ Gupta,⁶ and Santappa.⁷ In the course of our studies on the oxidation of organosulphur compounds with several oxidants, we have reported^{8,9} results for the detailed investigation of the kinetics of oxidation of alkyl aryl sulphides with potassium peroxodisulphate. Since both peroxodiphosphate and peroxodisulphate ions are iso-electronic and isostructural with almost equal oxidation potentials, it is relevant to study the oxidation of the sulphides with peroxodiphosphate. Incidentally a comparison may be drawn with the results derived from the kinetics of oxidation of the same sulphides with peroxodisulphate. This paper presents the results of the kinetics of oxidation of aryl methyl sulphides and alkyl phenyl sulphides with potassium peroxodiphosphate in 50% (v/v) aqueous acetic acid.

RESULTS AND DISCUSSION

The rate constants for different initial concentrations of peroxodiphosphate (PP) (1.0×10^{-3} – $3.0 \times 10^{-3}M$) and methyl phenyl sulphide (MPS) (1.002×10^{-2} – $3.007 \times 10^{-2}M$) at constant ionic strength (maintained by the addition of sodium perchlorate) and $[H^+]$ are presented in Table 1). Plots of $\log [PP]$ against time yielded straight lines, from which the pseudo-first-order rate constants (k_{ψ}) were calculated from the gradients. From the \log - \log plot of the rate constants and $[MPS]$, the order of reaction with respect to the concentration of MPS was found to be 1.03 ($r 0.999$, $s 0.01$). Further a plot of k_{ψ} versus $[MPS]$ gave a good straight line passing through the origin, showing that the reaction is second order.

Dependence on $[H^+]$.—The rate of oxidation of MPS by PP increases significantly with increasing $[H^+]$ by the added perchloric acid at constant ionic strength. A

plot of $\log k_{\psi}$ against $\log [H^+]$ gave a straight line with slope 1.06 ($r 0.991$, $s 0.02$) showing the first-order dependence in $[H^+]$. Further, the fact that the plot of k_{ψ} versus $[H^+]$ was found to be linear passing through the origin (Figure 1) shows that the reaction is completely acid-dependent.

Active Species.—The relative concentrations of the different species, *viz.* $P_2O_8^{4-}$, $HP_2O_8^{3-}$, $H_2P_2O_8^{2-}$, $H_3P_2O_8^{-}$, and $H_4P_2O_8$ as a function of pH has been discussed by Crutchfield.¹⁰ In the present study the pH has been maintained in the range 1–2 in which the following

TABLE 1

Pseudo-first-order* and second-order rate constants* for the reaction of MPS with PP at 35 °C: solvent 50% (v/v) aqueous acetic acid, $[H^+]_T 0.013 80M$, $I 0.2M$

$10^2 [MPS]/M$	$10^3 [PP]/M$	$10^5 k_{\psi}/s^{-1}$	$10^3 k/dm^3 mol^{-1} s^{-1}$
1.002	1.0	6.58 ± 0.29	6.56 ± 0.29
1.504	1.0	10.1 ± 0.45	6.70 ± 0.30
2.005	1.0	13.1 ± 0.59	6.54 ± 0.29
2.239	1.0	14.7 ± 0.66	6.55 ± 0.29
2.506	1.0	16.7 ± 1.05	6.65 ± 0.42
3.007	1.0	21.0 ± 0.94	6.99 ± 0.31
3.007	1.5	20.2 ± 0.90	6.73 ± 0.30
3.007	2.0	20.6 ± 1.30	6.85 ± 0.43
3.007	2.5	19.3 ± 0.87	6.43 ± 0.29
3.007	3.0	20.3 ± 0.85	6.72 ± 0.28

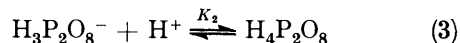
* The error quoted in k is the 95% confidence limit of the 'student t '.

three species, *viz.*, $H_2P_2O_8^{2-}$, $H_3P_2O_8^{-}$, and $H_4P_2O_8$, may be present in solution.¹⁰ Therefore the total concentration of PP is given by $[PP]_T = [H_2P_2O_8^{2-}] + [H_3P_2O_8^{-}] + [H_4P_2O_8]$. If all three species are considered to contribute to the rate with respect to PP, the rate expression is given by equation (1) where K_1 and K_2

$$\begin{aligned} \frac{-d[PP]_T}{dt} &= k_1[H_2P_2O_8^{2-}] + k_2[H_3P_2O_8^{-}] + k_3[H_4P_2O_8] \\ &= \frac{[PP]_T (k_1 + k_2K_1[H^+] + k_3K_1K_2[H^+]^2)}{1 + K_1[H^+] + K_1K_2[H^+]^2} \quad (1) \end{aligned}$$

represent the equilibrium constants for the protonation of $H_2P_2O_8^{2-}$ and $H_3P_2O_8^{-}$, respectively, as shown in reactions (2) and (3).

From a study of the oxidation of bromide ion by PP in aqueous perchloric acid medium, Gupta and his co-workers¹¹ were able to estimate and improve the values of the first and second dissociation constants ($K' = 1/K_2$ and $K'' = 1/K_1$) of $H_4P_2O_8$ given earlier by Crutchfield



and Edwards.¹² They estimated that the lowest value of the second dissociation constant is 40 and concluded that the first dissociation constant K' should be >40 . Therefore, it is possible to simplify the rate equation (1) neglecting the second and third terms in the denominator

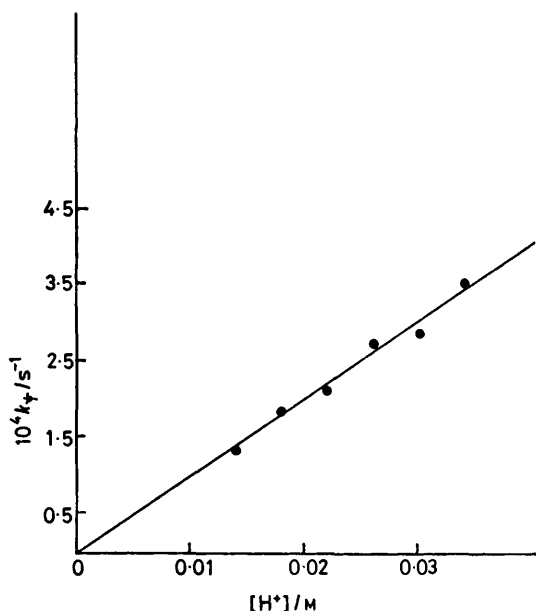


FIGURE 1 Effect of $[H^+]$ on the rate of oxidation of MPS by potassium peroxodiphosphate at 35 °C

in comparison to unity. Hence the rate equation (1) reduces to the numerator terms only.

The nature of the active PP species involved in the reaction may be arrived at on the basis of the dependence of the reaction rate on $[H^+]$. Thus the inference that $H_3P_2O_8^-$ is the active species becomes inescapable, because the plot of k_p versus $[H^+]$ was found to be linear passing through the origin (Figure 1) with a simple first-order dependence on $[H^+]$. It is also in accordance with the suggestion of Venturini *et al.*,¹³ that in the region of $[H^+]$ 0.01–0.7M only one kind of species, *viz.*, $H_3P_2O_8^-$ was responsible for the electrochemical reduction of PP.

Effect of Ionic Strength.—The logarithm of the rate constant of the reaction decreases linearly with an increase in the ionic strength of the medium (Table 2). The overall effect of ionic strength would be determined by equations (2) and (4). A decrease in rate on increasing the ionic strength is predicted for equation (2). Though one would expect a small effect of ionic strength for such equilibria, it is significant in our case. Further,

the rate-determining step (4) involves a reaction between an ion and a neutral molecule. The salt effect observed in such a case may be explained by the equation¹⁴ $\log_{10} k = \log_{10} k_0 + (b_A + b_B - b_T) \mu$. However, the overall effect of ionic strength on this reaction is determined by the combination of equations (2) and (4) and hence it is not possible to interpret the observed negative salt effect by any single equation.

Effect of Acrylonitrile.—Experiments conducted in the presence and absence of oxygen with the vinyl monomer acrylonitrile, had no effect on the rate in the oxidation of MPS and no visible polymerisation occurred during the reaction. Hence it is clear that the reaction does not

TABLE 2

Effect of ionic strength on the rate of oxidation of MPS by PP at 35 °C: [MPS] 0.019 47M, [PP] 0.001M, $[H^+]_T$ 0.013 80M in 50% (v/v) aqueous acetic acid

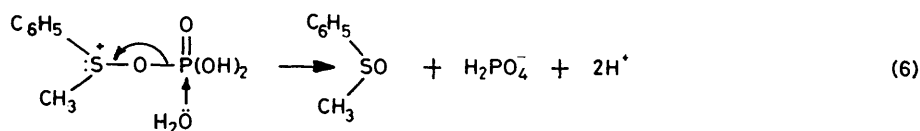
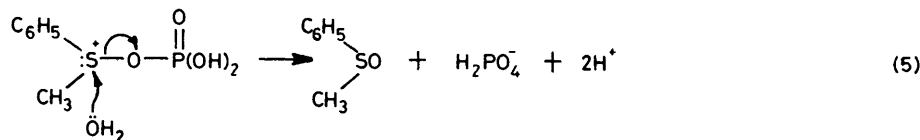
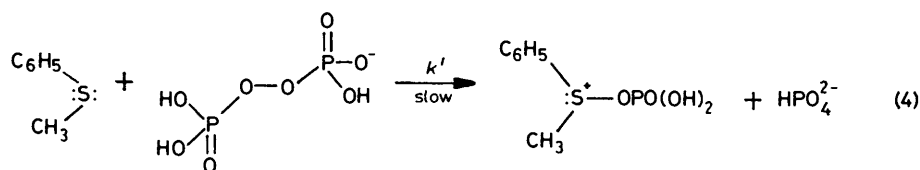
$10^2 I / M$	$10^5 k_p / s^{-1}$	$10^3 k / dm^3 mol^{-1} s^{-1}$
1.20	29.4 ± 1.86	15.1 ± 0.96
2.50	27.4 ± 1.22	14.1 ± 0.63
5.00	23.5 ± 1.99	12.1 ± 1.02
7.50	21.7 ± 0.96	11.1 ± 0.49
10.0	17.7 ± 0.76	9.07 ± 0.39
15.0	14.7 ± 0.93	7.57 ± 0.47
20.0	12.3 ± 0.73	6.32 ± 0.38

involve any free-radical intermediates derived from peroxodiphosphate ions. A similar observation has been reported by Edwards and his co-workers¹⁵ in the oxidation of propan-2-ol by PP.

Activation Parameters.—The dependence of rate constants on temperature was measured at three temperatures *viz.*, 35, 40, and 45 °C at constant $[H^+]$ and ionic strength. The experimental data fit the Arrhenius equation and the activation parameters for the aryl methyl sulphides studied are given in Table 3. The reaction is characterised by a low enthalpy of activation and an appreciable negative entropy of activation. The negative value of the entropy of activation suggests that the activated complex formed from the two reactants should have an exacting specificity of orientation.

Mechanism and Rate Law.—On the basis of the kinetic observations, and by analogy with the mechanism proposed for the oxidation of MPS with potassium peroxodisulphate,⁸ the polar mechanism involving reactions (4)–(6) may be envisaged. The intermediate formed in step (4) may decompose to give the sulphoxide by the attack of water as indicated in step (5) or (6). However, the question regarding the origin of the sulphoxide oxygen, whether from water or from peroxodiphosphate ion, has not been solved. Presumably the oxygen should originate from the solvent nucleophile water, rather than the peroxodiphosphate species, because the P–O bond is fairly stabilized by the d_p-p_π bonding making the removal of oxygen more difficult.¹⁶

The proposed mechanism is consistent with the following facts. (1) It follows overall second-order kinetics at constant $[H^+]$ and ionic strength which may be expressed by the rate law (7). (2) The reaction shows no indication of being free-radical in nature, since



it failed to induce polymerisation of acrylonitrile under nitrogen. (3) The entropy of activation is negative as expected for a bimolecular rate-determining step with

$$\begin{aligned} -\frac{d[\text{PP}]_{\text{T}}}{dt} &= k'[\text{H}_3\text{P}_2\text{O}_8^-][\text{MPS}] \\ &= k'K_1[\text{H}_2\text{P}_2\text{O}_8^{2-}][\text{H}^+][\text{MPS}] \\ &= k'K_1[\text{PP}]_{\text{T}}[\text{H}^+][\text{MPS}] \\ &= k[\text{PP}]_{\text{T}}[\text{MPS}] \end{aligned} \quad (7)$$

specific orientation of the reactants in the activated complex.

Substituent Effects.—An insight into the nature of the

any Hammett-type correlation exists for the oxidation of aryl methyl sulphides with PP. The reactivity pattern is brought out by two different correlations at 40 °C, one of $\log k$ with σ and the other of $\log k$ with σ^+ and/or σ^- correlation.* Since sulphur can act as an electron donor or acceptor depending upon the substituent *para* to the methylthio-group,¹⁷ we have used both σ^+ and σ^- simultaneously in the latter correlation. It may be pointed out here that in some reactions^{9,18,19} involving a sulphur centre, both σ^+ and σ^- have been employed simultaneously. Though a satisfactory correlation²⁰ is obtained with Hammett σ constants ($\rho -0.985$, $r 0.970$, $s 0.08$, confidence limit on $\rho \pm 0.16$) an excellent correl-

TABLE 3

Second-order rate constants and enthalpies and entropies of activation for the oxidation of $\text{XC}_6\text{H}_4\text{SMe}$ by PP *

No.	X	$10^3 k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$			$\Delta H^\ddagger/k \text{ mol}^{-1} \ddagger$	$-\Delta S^\ddagger/J \text{ K}^{-1} \text{ mol}^{-1}$ at 40 °C †
		35 °C	40 °C	45 °C		
(1)	H	6.67 ± 0.32	9.90 ± 0.44	14.2 ± 0.67	59.8 ± 7.6	92.9 ± 25
(2)	<i>p</i> -MeO	22.2 ± 0.99	32.4 ± 1.92	45.6 ± 2.19	55.9 ± 8.2	95.8 ± 27
(3)	<i>p</i> -Me	12.0 ± 0.58	17.9 ± 0.96	25.5 ± 1.45	59.0 ± 8.6	90.7 ± 28
(4)	<i>p</i> -Pr ^t	11.9 ± 0.57	16.4 ± 0.73	21.9 ± 2.30	47.3 ± 10	128 ± 35
(5)	<i>p</i> -F	7.20 ± 0.48	9.53 ± 0.81	13.4 ± 0.77	48.2 ± 11	130 ± 37
(6)	<i>m</i> -Me	7.41 ± 0.45	11.3 ± 0.79	16.9 ± 1.28	64.5 ± 11	76.6 ± 37
(7)	<i>m</i> -MeO	6.82 ± 0.48	9.60 ± 0.43	14.4 ± 0.64	58.3 ± 8.6	97.9 ± 28
(8)	<i>p</i> -Cl	6.07 ± 0.27	8.57 ± 0.55	13.6 ± 0.78	63.1 ± 9.0	83.5 ± 29
(9)	<i>p</i> -Br	4.71 ± 0.33	8.21 ± 0.52	11.5 ± 0.54	70.6 ± 9.8	59.7 ± 32
(10)	<i>m</i> -Cl	4.24 ± 0.28	5.77 ± 0.36	9.26 ± 0.41	61.0 ± 9.5	93.5 ± 31
(11)	<i>p</i> -Ac	2.38 ± 0.14	3.50 ± 0.16	5.87 ± 0.45	70.9 ± 9.8	65.9 ± 32
(12)	<i>p</i> -CO ₂ H	2.46 ± 0.16	3.73 ± 0.45	5.48 ± 0.20	61.9 ± 12	93.7 ± 40
(13)	<i>p</i> -NO ₂	1.45 ± 0.23	2.41 ± 0.10	3.88 ± 0.25	79.2 ± 14	42.8 ± 48

* General conditions: [Sulphide]/[PP] *ca.* 20 in 50% (v/v) aqueous acetic acid at *I* 0.2M and $[\text{H}^+]_{\text{T}}$ 0.013 80M.

† The observed range of experimental ΔH^\ddagger is >28. The precision of ΔH^\ddagger and ΔS^\ddagger values were calculated using the method of Petersen *et al.*²⁰

transition state and hence the mechanism can also be gained from an analysis of the substituent effects on the course of the oxidation. The effect of substituents on the rate of oxidation has been studied by employing a number of *meta*- and *para*-substituted phenyl methyl sulphides. The rate of the reaction is accelerated by electron-releasing and retarded by electron-withdrawing substituents (Table 3). It is of interest to find out if

ation is found to exist when σ^+ and/or σ^- values are plotted against $\log k$ ($\rho -0.618$, $r 0.994$, $s 0.03$, confidence limit on $\rho \pm 0.04$). The negative ρ value indicates that the nucleophilic sulphur atom of the sulphide is more positively charged in the transition state of the rate-determining step of the oxidation reaction than it is in the reactant, and this is consistent

* Appropriate σ^+ or σ^- values were used as cited in ref. 9.

only with step (4) as rate determining. The reaction constant ρ has also been evaluated at three temperatures and is inversely proportional to the temperature (ρ -0.641 , -0.619 , and -0.576 , at 35 , 40 , and 45 °C, respectively), as expected.²¹ The low ρ value observed in this reaction may be due to the weak electrophilic character of PP which is similar to peroxodisulphate.⁹

Isokinetic Relationships.—Generally the Hammett correlation appears to apply to a reaction series in which either ΔS^\ddagger is constant or in which the variation in ΔS^\ddagger is linearly related to changes in ΔH^\ddagger .²²⁻²⁵ In the latter case these two variables are correlated²⁵⁻²⁸ by equation

$$\Delta H^\ddagger = \Delta H_0^\ddagger + \beta \Delta S^\ddagger \quad (8)$$

(8) where β is the isokinetic temperature. It can be evaluated from the slope of the plot of ΔH^\ddagger against ΔS^\ddagger . Since the observed range of experimental ΔH^\ddagger value is >28 , the relation between ΔH^\ddagger and ΔS^\ddagger can be assumed to be valid²⁹ in the present study. The value of β obtained from such a plot, for the oxidation of aryl methyl sulphides employing the data given in Table 3, is found to be 354 K (r 0.985 , s 0.04). Better values of β can be obtained from a log-log plot of the rate constants at two different temperatures as advocated by Exner.³⁰ The value of β evaluated in this manner from the plot of $\log k$ (45 °C) against $\log k$ (35 °C) is 445 K (r 0.994 , s 0.03). However, the isokinetic temperatures obtained from both methods are above the experimental temperatures and hence this reaction series may be considered to be under the control of ΔH^\ddagger , according to the concept of Bunnett.³¹ The good correlation obtained in the iso-

TABLE 4

Second-order rate constants for the oxidation of aryl phenyl sulphides with PP at 40 °C and relative rates of oxidation *

Sulphide	$10^3 k / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	Relative rates of oxidation	
		PP	$\text{S}_2\text{O}_8^{2-}$ †
PhSMe	9.90 ± 0.44	100	100
PhSEt	6.57 ± 0.50	66	39
PhSPr ⁿ	5.52 ± 0.38	56	32
PhSPr ⁱ	3.20 ± 0.14	32	15
PhSBu ^t	0.59 ± 0.06	6.0	1.7

* General reaction condition: $[\text{Sulphide}]/[\text{PP}]$ ca. 20 in 50% (v/v) aqueous acetic acid at I 0.2M and $[\text{H}^+]_{\text{T}}$ 0.0138M .
† Values from ref. 9.

kinetic relationship also leads to the conclusion²⁵ that the mechanism of the reaction between PP and all the aryl methyl sulphides is one and the same. It may be stated here, however, that current views³²⁻³⁵ do not attach much significance to isokinetic temperatures, though a linear correlation is usually a necessary condition for the validity of the Hammett equation.

Oxidation of Alkyl Phenyl Sulphides.—The oxidation of alkyl phenyl sulphides $\text{C}_6\text{H}_5\text{SR}$ ($\text{R} = \text{Me, Et, Pr}^n, \text{Pr}^i, \text{and Bu}^t$) with PP was also studied. The rate data are given in Table 4. The rate decreases in the order $\text{PhSMe} > \text{PhSEt} > \text{PhSPr}^n > \text{PhSPr}^i > \text{PhSBu}^t$. If the contributions of the $+I$ effect of the alkyl groups predominate over the steric effect offered by the increasing bulk-

ness of the alkyl groups, one would expect a reverse order in the rate of the reaction mentioned above. But the results show clearly that the reaction is sensitive to steric congestion at the reaction centre. Thus the steric factor seems to play a dominant role rather than the $+I$ effect in this oxidation. Hence, we tried to correlate the $\log k$ values against the recently evaluated steric factor³⁶ ξ_r which reflects only the steric repulsion of the groups R by a symmetrical counterpart. A linear relationship is observed (r 0.979 , s 0.11). The view that step (4) is rate-determining in the oxidation process also receives support from the existence of the steric effect.

Comparison with Peroxodisulphate Oxidation of the Sulphides.—The oxidations of alkyl aryl sulphides by both peroxodiphosphate and peroxodisulphate ions take place by nucleophilic displacement of the sulphide sulphur on the peroxide oxygen of the two peroxy-salts. The reactions resemble each other in the following aspects. (a) Both follow second-order kinetics. (b) The two reactions proceed by a non-radical polar mechanism, as the rates are unaffected by radical-trapping agents. (c) Both are characterised by a low enthalpy of activation and an appreciable negative entropy of activation. (d) The structural effects on the rate of oxidation of sulphides with peroxodiphosphate are similar to those for the rates of oxidation of the corresponding sulphides with peroxodisulphate. This is also brought out by the existence of a linear free energy relationship (Figure 2) of a log-log plot of the rate

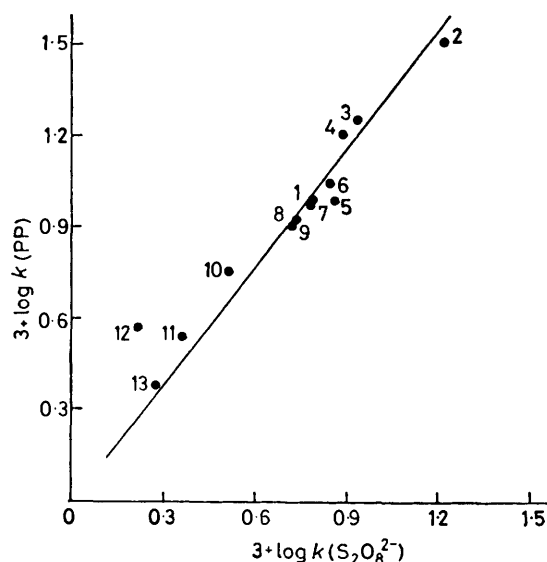


FIGURE 2 Correlation of $\log k$ of PP oxidation with $\log k$ of $\text{S}_2\text{O}_8^{2-}$ for the oxidation of aryl methyl sulphides (1)–(13) (see Table 3) at 40 °C, slope 1.05 , r 0.969 , s 0.08

constants of peroxodiphosphate and peroxodisulphate reactions (Slope 1.05 , r 0.969 , s 0.08), though the reactions were carried out in different conditions.* If the two transition states are related to each other, then

* In the peroxodisulphate reactions 50% (v/v) aqueous alcohol was used as solvent with ionic strength 0.015M .

a slope close to unity is a clear indication that the mechanisms for the two reactions are very similar (*i.e.*, it is quite likely that the O-O bond in the peroxy-salt is being cleaved in both transition states). (e) The steric effect observed on the rate of oxidation of both reactions demonstrates the same trend (Table 4).

The essential differences observed between the two reactions are (a) the peroxodiphosphate reaction is acid-catalysed while the peroxodisulphate reaction is not, and (b) the salt effect is negative and considerable in the peroxodiphosphate reaction while it is negligibly small and positive in the peroxodisulphate reaction. These two differences may arise mainly due to the protonation equilibrium of step (2) in the reactions.

EXPERIMENTAL

Materials.—Tetrapotassium peroxodiphosphate (FMC Corporation) was used after repeated recrystallisation from methanol-water. Sodium perchlorate (Merck) and 60% perchloric acid (Merck) were used as such. All the sulphides used for kinetic measurements were prepared by known methods and are reported elsewhere.^{8,9} The purity was checked by spectroscopic methods and t.l.c. All the other chemicals used were of AnalaR grade.

Solvents.—Doubly distilled water was employed throughout, the second distillation being from potassium permanganate. Acetic acid was purified by the procedure of Orton and Bradfield.³⁷

Kinetics.—The kinetic studies were carried out in 50% (v/v) aqueous acetic acid at constant ionic strength (maintained by the addition of sodium perchlorate) and at constant [H⁺] under pseudo-first-order conditions with a ca. 20-fold excess of substrate over oxidant concentration. The alkalinity of peroxodiphosphate was always taken into account in the calculation of [H⁺]. The reaction was followed by estimating the unchanged peroxodiphosphate by the iodometric procedure of Gupta and his co-workers.³⁸ Reactions were followed to 60–70% completion; reproducible results giving good first-order plots ($r > 0.995$) were obtained for reactions run in duplicate or triplicate and at least three different temperatures. The kinetic constants k_{ψ} were calculated by the least-squares method using a Micro 2200 computer (Hindustan Computers). The precision of the k values is given in terms of the 95% confidence limit, calculated with 'student t .' From the k_{ψ} values the second-order rate constants k were obtained ($k = k_{\psi}/[\text{Substrate}]$).

Stoichiometry.—The stoichiometry of oxidation was determined by allowing an excess of peroxodiphosphate to react with the substrate overnight and the unchanged peroxodiphosphate was estimated. The stoichiometry is found to be 1 : 1 and the reaction has been shown to proceed quantitatively according to equation (9).



Product Analysis.—The reaction mixture was analysed by t.l.c. as reported earlier.^{8,9} It was confirmed that sulphoxide was the only product formed during the reaction under the present experimental conditions which is also confirmed by the fact that the oxidation of sulphoxide³⁹ to sulphone is extremely slow in comparison to the oxidation of sulphide (second-order rate constants for the

oxidation of methyl phenyl sulphide and methyl phenyl sulphoxide are 9.95×10^{-3} and $0.123 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively, under identical experimental conditions).

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