

Mechanism of the oxidation of alkyl aryl and diphenyl sulphoxides by peroxomonosulphate

R SUTHAKARAN, P SUBRAMANIAM and C SRINIVASAN*

School of Chemistry, Madurai Kamaraj University, Madurai 625 021, India

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Abstract. Detailed kinetic investigations of the oxidation of methyl phenyl sulphoxide and diphenyl sulphoxide by peroxomonosulphate in aqueous acetic acid medium reveal that the reactions are first-order, both in the sulphoxide and in the oxidant. Studies with substituted phenyl methyl sulphoxides and 4,4'-disubstituted diphenyl sulphoxides show that electron-releasing groups accelerate the rate of oxidation and electron-withdrawing groups retard it. A fair correlation between $\log k_2$ and Hammett substituent constants has been observed in the two series. The mechanism proposed involves the rate-determining nucleophilic attack of the sulphoxide sulphur at the outer terminal peroxy oxygen atom of HSO_5^- .

Keywords. Peroxomonosulphate; oxidation of sulphoxides; structure-reactivity relationship.

1. Introduction

The synthetic utility of potassium hydrogen persulphate or potassium peroxomonosulphate (Kennedy and Stock 1960) as an oxidant has been studied in detail. The chemoselective oxidation of sulphides to sulphones by peroxomonosulphate (PMS) have been noticed (Troost and Curran 1981). PMS has been recently employed for the epoxidation of *trans*-cinnamic acid (Curci *et al* 1980) and alkenes (Bloch *et al* 1985). However, there are only a few kinetic studies with PMS as the oxidant. The kinetics of oxidation of halide (Fortnum *et al* 1960; Secco and Venturini 1976), nitrite (Edwards and Muller 1962), thiocyanate ion (Smith and Wilson 1966, 1967), alkyl thiocyanates (Bridgart and Wilson 1971), azide and azidopentamminechromium(III) (Thompson *et al* 1979), oxovanadium and peroxovanadium (Thompson 1981, 1982), amino acids (Ramachandran and Vivekanandam 1984; Ramachandran *et al* 1984) and dimethyl sulphoxide (Pandurengan and Maruthamuthu 1981) have been investigated. Because aromatic sulphoxides can act as either nucleophiles or electrophiles in the kinetics of peroxobenzoic acid oxidations (Curci and Modena 1964), a detailed kinetic study on the oxidation of sulphoxides would be of great interest with PMS. In this paper we report our results on the kinetics of oxidation of methyl phenyl sulphoxide (MPSO), diphenyl sulphoxide (DPSO), several substituted phenyl methyl sulphoxides and diphenyl sulphoxides by PMS. A plausible mechanism, based on the kinetic results, has also been proposed.

* To whom all correspondence should be addressed

2. Experimental

2.1. Materials

All the substituted phenyl methyl sulphoxides were prepared from the corresponding sulphides by chromium trioxide oxidation (Baliah and Satyanarayana 1978). Methyl *p*-nitrophenyl sulphoxide was obtained by the oxidation of corresponding sulphide with nitric acid (Zincke and Lenhardt 1913). *p*-Acetylphenyl methyl sulphoxide was prepared by the potassium peroxodisulphate oxidation of the corresponding sulphide (Srinivasan *et al* 1986). The Friedel-Crafts reaction of benzene with thionyl chloride furnished diphenyl sulphoxide and similarly disubstituted diphenyl sulphoxides were obtained from substituted benzenes (Cumber *et al* 1965; Leonard and Sutton 1948; Sugaswa and Sakurai 1940). 4,4'-Dinitrodiphenyl sulphoxide was obtained by the hydrogen peroxide oxidation of the corresponding sulphide (Szmant and McIntosh 1951). All the sulphoxides were purified by distillation or recrystallization before kinetic use. The purity of the sulphoxides was established by means of sharp melting behaviour with solids, single spot on TLC and by spectral studies. Doubly distilled water was used throughout, the second distillation being from permanganate. Peroxomonosulphate, $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ (Oxone), sulphuric acid (AR) and potassium bisulphate (GR) were used as such. Acetic acid was purified by refluxing with chromium trioxide (Orton and Bradfield 1924).

2.2 Kinetic measurements

The oxidation studies with aryl methyl sulphoxides were conducted in 50% acetic acid-50% water (v/v) under pseudo first-order conditions with a ten-fold excess of the substrate over that of the oxidant concentration. The studies with 4,4'-disubstituted diphenyl sulphoxides were carried out in 80% acetic acid-20% water (v/v) due to their poor solubility in 50% acetic acid-50% water (v/v) medium. The progress of the reaction was followed by estimating the unconsumed PMS iodometrically by taking aliquot at regular intervals of time. The pseudo first-order rate constants (k_1) were calculated from the slope of the linear plot of $\log(a-x)$ vs time by the method of least-squares using a IBM 1130 computer. The correlation coefficient for each run is > 0.995 . Straight lines were generally obtained for at least 60% of the reaction. The second-order rate constants were obtained from the relation $k_2 = k_1/[\text{substrate}]$.

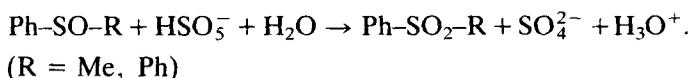
2.3 Product analysis

The reaction mixture from actual kinetic run was neutralised with sodium carbonate, the solution was evaporated to dryness and ether extracted. Removal of ether gave solid product. On the basis of m.p. and TLC methyl phenyl sulphone and diphenyl sulphone were identified as the final products in the oxidations of MPSO and DPSO respectively.

2.4 Reaction stoichiometry

The stoichiometry of the reaction was determined by estimating the unreacted PMS after completion of the reaction by allowing an excess of it to react with substrate

and was found to be 1:1 in both aryl methyl and diaryl sulphoxides. Thus the overall reaction is



3. Results and discussion

3.1 Oxidation of MPSO

The kinetic studies were carried out under pseudo first-order conditions in the presence of MPSO in 50% acetic acid-50% water (v/v) mixture. Plots of $\log [\text{PMS}]$ against time were linear with slopes that were independent of the initial concentration of PMS, indicating the first-order dependence on the oxidant. The constant pseudo first-order constants (k_1) (see table 1) at different initial concentrations of PMS also reveal the first-order dependence on PMS. The linear dependence of $\log k_1$ on $\log [\text{MPSO}]$ with a slope of 1.05 ($r = 0.999$) and the constant values of second-order rate constants at different concentrations of $[\text{MPSO}]$ (table 1) indicate a first-order dependence on MPSO. The rate law may, therefore, be expressed as

$$-\frac{d[\text{PMS}]}{dt} = k_2[\text{MPSO}][\text{PMS}].$$

The rate of oxidation is almost acid independent ($[\text{H}^+]$ was maintained by the addition of H_2SO_4 , see table 2). The kinetic data in table 2 also show that the rate is unaffected by the change in the ionic strength of the medium maintained by the addition of sodium bisulphate. This may be due to the reaction between an ion and

Table 1. Pseudo-first-order and second-order rate constants for the oxidation of MPSO and DPSO with PMS in 50% (v/v) aqueous acetic acid^a.

$10^2[\text{Sulphoxide}]$ (M)	$10^3[\text{PMS}]$ (M)	MPSO at 30°C		DPSO at 27.5°C	
		$10^4 k_1 (\text{sec}^{-1})$	$10^2 k_2 (\text{M}^{-1} \text{sec}^{-1})$	$10^4 k_1 (\text{sec}^{-1})$	$10^2 k_2 (\text{M}^{-1} \text{sec}^{-1})$
0.75	0.75	5.15 ± 0.25	6.86 ± 0.33	1.90 ± 0.16	2.53 ± 0.21
1.00	0.75	6.35 ± 0.32	6.35 ± 0.32	2.67 ± 0.14	2.67 ± 0.14
1.50	0.75	9.79 ± 0.53	6.52 ± 0.35	3.99 ± 0.18	2.66 ± 0.12
2.00	0.75	13.2 ± 0.88	6.59 ± 0.44	5.31 ± 0.55	2.66 ± 0.28
2.50	0.75	16.9 ± 1.2	6.77 ± 0.48	6.70 ± 0.53	2.68 ± 0.21
3.00	0.75	19.5 ± 0.70	6.51 ± 0.23	7.93 ± 0.35	2.64 ± 0.12
4.00	0.75	26.9 ± 1.0	6.74 ± 0.26	9.25 ± 0.33	2.31 ± 0.08
5.00	0.75	32.4 ± 1.6	6.48 ± 0.32	11.7 ± 0.65	2.35 ± 0.13
1.50	0.50	9.87 ± 0.63	6.58 ± 0.42	3.78 ± 0.48	2.52 ± 0.32
1.50	1.00	10.3 ± 0.41	6.84 ± 0.27	3.93 ± 0.12	2.62 ± 0.08
1.50	1.25	9.79 ± 0.37	6.52 ± 0.25	3.95 ± 0.28	2.63 ± 0.19
1.50	1.50	10.1 ± 0.48	6.75 ± 0.32	4.18 ± 0.05	2.79 ± 0.03

^a $[\text{H}_2\text{SO}_4] = 0.10 \text{ M}$; $I = 0.60 \text{ M}$. The error quoted in k is the 95% confidence limit of Student's t -test (Srinivasan *et al* 1982).

Table 2. Effect of varying $[H^+]$, I , and percentage of solvent composition on the rate of oxidation^a.

10 $[H_2SO_4]$ (M)	MPSO ^{b,c}		DPSO ^{c,d}		I (M)	MPSO ^{b,e}		DPSO ^{d,e}		AcOH-H ₂ O (v/v)	MPSO ^{b,f}		DPSO ^{d,f}	
	$10^4 k_1$ (sec ⁻¹)		$10^4 k_1$ (sec ⁻¹)		$10^4 k_1$ (sec ⁻¹)									
0.25	5.12 ± 0.16	1.92 ± 0.02	0.40	5.67 ± 0.21	2.03 ± 0.10	10-90	10.6 ± 0.69	4.87 ± 0.30						
0.50	5.18 ± 0.14	2.00 ± 0.07	0.60	5.15 ± 0.25	1.90 ± 0.16	30-70	7.77 ± 0.53	2.53 ± 0.18						
1.00	5.15 ± 0.25	1.90 ± 0.16	0.70	5.38 ± 0.09	1.87 ± 0.10	50-50	5.15 ± 0.25	1.90 ± 0.16						
1.50	5.55 ± 0.21	2.05 ± 0.16	0.90	5.18 ± 0.18	1.83 ± 0.09	70-30	4.41 ± 0.28	1.65 ± 0.07						
1.90	5.75 ± 0.21	2.27 ± 0.09	1.00	5.18 ± 0.07	1.90 ± 0.12									

^a[Sulphoxide] = 7.5×10^{-3} M; [PMS] = 7.5×10^{-4} M; ^b $T = 30^\circ\text{C}$; ^c $I = 0.60$ M; solvent 50:50; AcOH-H₂O (v/v); ^d $T = 27.5^\circ\text{C}$;
^e $[H_2SO_4] = 0.10$ M; solvent 50:50 AcOH-H₂O (v/v); ^f $I = 0.60$ M; $[H_2SO_4] = 0.10$ M.

a neutral molecule in the rate-determining step. The oxidation rate increases with decrease in the percentage of acetic acid in the medium (table 2) indicating a possible formation of a charged activated complex in the transition state which is more hydrated than those of the reactants. Such a solvent effect is observed in the oxidation of methyl phenyl sulphoxide by N-bromo-succinimide (Srinivasan *et al* 1983), alkyl aryl sulphides by peroxodisulphate (Kuthalingam 1980; Sundararajan 1981) and phenyliodosodiacetate (Srinivasan *et al* 1982), and phenylmercaptoacetic acids by peroxodisulphate (Srinivasan and Pitchumani 1979). In the Cr(VI) oxidation of aryl methyl (Baliah and Satyanarayana 1978) and diaryl sulphoxides (Srinivasan *et al* 1981) and of sulphides (Srinivasan *et al* 1985) the formation of charge-separated complex in the rate-limiting step has been excluded as the rate constant increases with increase in the content of the acetic acid in the medium in these oxidations. Since the rate is also not influenced by the addition of acrylonitrile, a free radical mechanism has been excluded.

3.2 Oxidation of DPSO

Our interest in the oxidation of DPSO and substituted diphenyl sulphoxides stems from some of our recent interesting observations with MPSO and DPSO in certain oxidations. In the peroxodiphosphate (Srinivasan and Rajagopal 1979; Rajagopal 1984) and N-bromosuccinimide oxidations (Srinivasan *et al* 1983) of MPSO, the reaction is first-order in substrate in each case, while zero-order dependence is observed in DPSO in its reactions with the two oxidants. But with both cases the order with respect to the oxidant is one. In contrast, the oxidations of MPSO and DPSO by Cr(VI) (Baliah and Satyanarayana 1978; Srinivasan *et al* 1981) and by peroxobenzoic acid (Curci and Modena 1966; Curci *et al* 1966) follow second-order kinetics.

Detailed studies with DPSO in 50% acetic acid-50% water (v/v) indicate that the order with respect to each reactant is unity as evidenced by the linearity of the plot of $\log(a-x)$ vs time, constant pseudo first-order rate constants at different initial [PMS] and by the constant k_2 values at different initial [DPSO] (table 1). A plot of $\log[\text{DPSO}]$ vs $\log k_1$ is linear with a slope of 1.03 ($r = 0.999$). As observed with MPSO, the reaction rate is not influenced by the variations in $[\text{H}^+]$ and ionic strength and the rate constants decrease with decrease in the percentage of water (table 2).

3.3 Substituent effects

The structure-reactivity relationship has been examined by studying the rates of PMS oxidation of several substituted phenyl methyl sulphoxides and 4,4'-disubstituted diphenyl sulphoxides at three temperatures (tables 3 and 4). The data in tables 3 and 4 reveal that while electron-releasing substituents increase the rate of oxidation, electron-withdrawing substituents retard it. The correlation of $\log k_2$, with Hammett substituent constants, σ , is only fair in the two series ($\rho = -0.40$, $r = 0.957$, $s = 0.04$, 95% confidence limit on $\rho = \pm 0.10$ for aryl methyl sulphoxides at 30° and $\rho = -0.40$, $r = 0.981$, $s = 0.06$, 95% confidence limit on $\rho = \pm 0.09$ for substituted diphenyl sulphoxides at 27.5°). The use of σ^+/σ^- has not improved the correlation. The nearly identical ρ values for the two series of sulphoxides show that in both cases the electron deficient transition state almost

Table 3. Second-order rate constants and enthalpies and entropies activation for the oxidation of $XC_6H_4SOCH_3$ by PMS^a.

X	$10^2 k_2 (M^{-1} sec^{-1})$			$\Delta H^\ddagger (KJ mol^{-1})$	$-\Delta S^\ddagger (JK^{-1} mol^{-1})$
	10°C	20°C	30°C		
H	1.72 ± 0.10	3.81 ± 0.16	6.86 ± 0.33	54.3 ± 3.6	88.0 ± 13
<i>p</i> -MeO	2.59 ± 0.08	5.22 ± 0.12	10.8 ± 0.37	56.2 ± 2.1	78.1 ± 7.7
<i>p</i> -Me	2.12 ± 0.07	4.17 ± 0.06	8.14 ± 0.24	52.9 ± 2.0	91.4 ± 7.2
<i>p</i> -Et	1.98 ± 0.07	4.07 ± 0.24	8.48 ± 0.73	57.0 ± 4.3	77.4 ± 16
<i>p</i> -Br	1.64 ± 0.12	3.44 ± 0.12	6.36 ± 0.49	46.6 ± 4.4	114 ± 16
<i>p</i> -Cl	1.56 ± 0.07	3.03 ± 0.20	5.71 ± 0.33	50.8 ± 4.0	101 ± 15
<i>p</i> -COCH ₃ ^b	1.28 ± 0.09	2.92 ± 0.19	4.84 ± 0.19	45.8 ± 4.2	119 ± 15
<i>m</i> -Cl	0.933 ± 0.03	2.52 ± 0.19	4.32 ± 0.33	53.3 ± 4.4	94.9 ± 16
<i>p</i> -NO ₂	0.821 ± 0.03	1.95 ± 0.03	3.77 ± 0.24	53.7 ± 2.8	95.0 ± 10

^a [Sulphoxide] = 7.5×10^{-3} M; [PMS] = 7.5×10^{-4} M; [H₂SO₄] = 0.10 M; *I* = 0.60 M; solvent 50:50 AcOH-H₂O (v/v). ^bThe Bayer-Villiger oxidation has been ruled out as acetophenone was not oxidised under our experimental conditions.

Table 4. Second-order rate constants and enthalpies and entropies of activation for the oxidation of disubstituted diphenyl sulphoxides by PMS^a.

Sulphoxide	$10^2 k_2 (M^{-1} sec^{-1})$			$\Delta H^\ddagger (KJ mol^{-1})$	$-\Delta S^\ddagger (JK^{-1} mol^{-1})$
	12.5°C	27.5°C	37.5°C		
Diphenyl	0.946 ± 0.03	2.43 ± 0.12	5.43 ± 0.24	48.8 ± 2.5	99.0 ± 8.9
4,4'-Diacetamido-diphenyl	1.77 ± 0.09	3.92 ± 0.09	6.39 ± 0.30	35.7 ± 2.4	153 ± 8.6
4,4'-Dimethyl-diphenyl	1.37 ± 0.08	3.89 ± 0.16	6.78 ± 0.28	45.3 ± 2.8	122 ± 10
4,4'-Difluoro-diphenyl	0.960 ± 0.03	2.67 ± 0.16	5.53 ± 0.47	49.4 ± 3.5	111 ± 13
4,4'-Dichloro-diphenyl	0.733 ± 0.02	2.25 ± 0.13	4.38 ± 0.32	50.5 ± 3.0	109 ± 11
4,4'-Dibromo-diphenyl	0.710 ± 0.03	2.12 ± 0.14	3.89 ± 0.18	48.3 ± 3.2	117 ± 12
4,4'-Dinitro-diphenyl	0.256 ± 0.03	0.693 ± 0.03	1.09 ± 0.03	40.5 ± 3.7	152 ± 13

^a[Sulphoxide] = 7.5×10^{-3} M; [PMS] = 7.5×10^{-4} M; [H₂SO₄] = 0.10 M; *I* = 0.40 M; solvent 80:20 AcOH-H₂O (v/v).

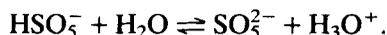
resembles each other. However, the low ρ values point out that the transition state cannot be as electron-deficient as pictured for electrophilic aromatic substitution.

The activation parameters for the oxidation of the two series of sulphoxides are also listed in tables 3 and 4. In both series the observed range of experimental ΔH^\ddagger value is $> 2\delta$ i.e. the error criterion (Petersen *et al* 1961; Wiberg 1964) is satisfied and hence the relation between ΔH^\ddagger and ΔS^\ddagger can be assumed to be valid. The linear relationship between ΔH^\ddagger and ΔS^\ddagger is satisfactory ($r = 0.984$ for aryl methyl

sulphoxides and $r = 0.963$ for diphenyl sulphoxides) suggesting that the oxidation occurs for all substrates by a similar mechanism in each series.

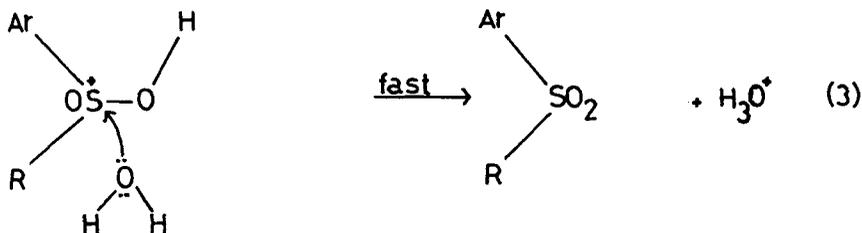
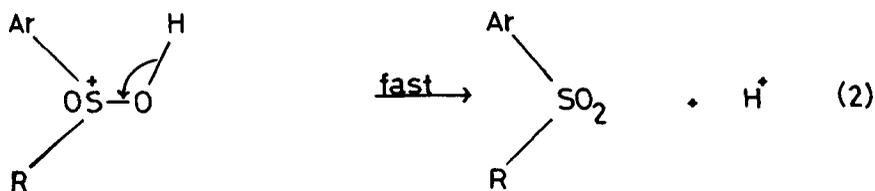
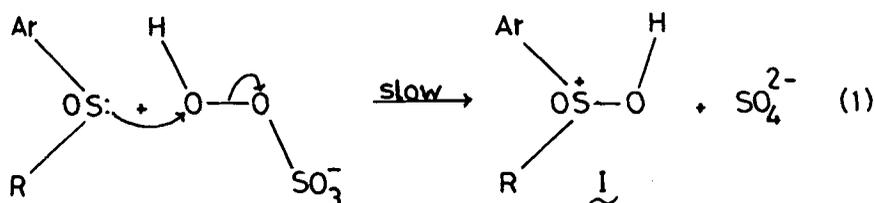
3.4 Mechanism of oxidation

In aqueous solution, peroxomonosulphate ion mainly exists as HSO_5^- , a weak acid with an ionisation constant 4×10^{-10} . However, in alkaline medium the concentration of HSO_5^- is much low (Ogata and Tabushi 1958). It has been reported that around $\text{pH} = 10$, HSO_5^- exists principally as SO_5^{2-} (Ball and Edwards 1956),



The absence of any effect on the rate of oxidation on the addition of a strong acid indicates (i) SO_5^{2-} is not the active species and (ii) HSO_5^- is the active species as the first ionization of peroxomonosulphuric acid lies in the very high acid region (Ball and Edwards 1956). Because of the unsymmetrical nature of the peroxide link, HSO_5^- is very reactive to strong nucleophiles (Ball and Edwards 1956).

Scheme 1.



$\text{R} = \text{CH}_3$ or aryl

In the proposed mechanism (scheme I) it is envisaged that the rate-determining step involves the nucleophilic attack of sulphoxide sulphur at the outer terminal peroxy oxygen atom of HSO_5^- to form an intermediate (I) analogous to the mechanism suggested for the peroxodisulphate oxidation of sulphides (Arumugam *et al* 1978; Srinivasan *et al* 1978) and to the general mechanism proposed for many peroxide reactions (Edwards 1962). As addition of potassium sulphate has not influenced the rate constant, it is concluded that (1) is not reversible. The intermediate (I) decomposes to give the sulphone with a loss of proton. The formation of the sulphonium ion intermediate (I) in the slow step accounts for the observed substituent effect and solvent effect. In the reactions of peroxomonosulphate with azidopentamminechromium(III) and with azide employing H_2O^{18} , $\text{O}_3^{18}\text{SO}^{18}\text{OH}^-$ (non-terminally labelled) and $\text{O}_3\text{SQO}^{18}\text{H}^-$ (terminally labelled), it has been shown that the reactions proceed by transfer of a terminal peroxide oxygen of the peroxomonosulphate to the reactants (Thompson *et al* 1979). It has also been demonstrated that Caro's acid is the source of oxygen in the oxidation of nitrite to nitrate (Anber and Taube 1954), and of phosphite to phosphate (Lunenok-Burmakina *et al* 1968). The intermediate (I) may also decompose to give the sulphone by the attack of water as shown in (3). This possibility is excluded as it has been reported (Gragerov and Levit 1963) that the treatment of diphenyl sulphide with a solution of ethanol, acetic acid, H_2O^{18} and peroxomonosulphate for 5 hours at 0° gave diphenyl sulphoxide devoid of O^{18} ; similar oxidation at $20-25^\circ$ gave diphenyl sulphone devoid of O^{18} . It is, therefore, concluded that the source of oxygen in the present study is PMS itself.

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