Mechanism of permanganate ion oxidation of diaryl sulphoxides – A kinetic study

S RAJAGOPAL,* GEETHA SIVASUBRAMANIAN, R SUTHAKARAN and C SRINIVASAN[a]

School of Chemistry, Madurai Kamaraj University, Madurai 625021, India
[a]Department of Materials Science, Madurai Kamaraj University, Madurai 625021, India

Abstract. The oxidation of 4,4'-disubstituted diphenyl sulphoxides by potassium permanganate on Hammett type correlations give a small positive ρ value (0·34). This is in contrast to the oxidation of aryl methyl sulphides ($\rho = -1·36$) by the permanganate ion. On the basis of rate data a mechanism of nucleophilic attack of MnO_4^- on the substrate has been proposed.

Keywords. Diaryl sulphoxides; permanganate oxidation; kinetics and mechanism.

1. Introduction

Although permanganate ion oxidation of sulphides has been used in synthesis (Bordwell and Cooper 1952), its use as an oxidant in the kinetics of oxidation of organic sulphur compounds has been very limited. Recently Banerji (1988) has investigated the kinetics and mechanism of oxidation of divalent organic sulphides by permanganate ions. A mechanism involving a rate-determining electrophilic oxygen transfer from permanganate ion to the sulphide has been proposed,

$$RSR' + MnO_4^- \longrightarrow \left[\begin{array}{c} R \end{array} \right] \longrightarrow RSR' + MnO_3^- \quad (1)$$
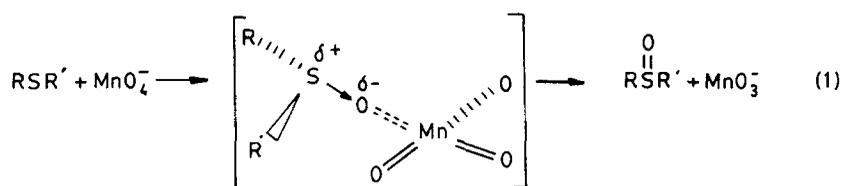
Organic sulphoxides are unique examples in oxidation reactions as they may behave either as electrophiles or nucleophiles during oxidation. Peroxobenzoic acid oxidation of p–X–$C_6H_4SOC_6H_5$ to the corresponding sulphones at low pH, where the peroxo acid is not dissociated, proceeds with the typical features of an electrophilic process ($\rho = -0·54$). On the other hand at higher pH values (> 10) the oxidation is characterised by a positive ρ value ($+0·71$) (Cerniani and Modena 1959; Curci and Modena 1963, 1965, 1966; Curci et al 1966, 1977). On the basis of the kinetic evidence, it has been suggested that sulphoxides are oxidised electrophilically by undissociated

---

* For correspondence

peroxoacid at low pH and nucleophilically by its anion at higher pH. The general scheme for the alkaline oxidation is

$$RCO_3^- + S{=}O \rightarrow [RCO_2{-}O{-}S{-}O] \rightarrow RCO_2^- + SO_2. \qquad (2)$$
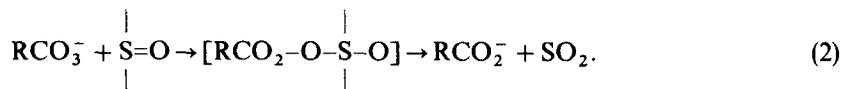
Because of the polarisation of the S–O linkage in sulphoxides, the decreased electron availability on the sulphur atom lowers the reactivity of sulphoxides as compared to that of corresponding sulphides. Structural aspects on reactivity are similar to those observed in sulphides but specific solvation effects are more important in the sulphoxides. However, a few exceptions have been observed recently wherein sulphoxides react faster than sulphides towards the same oxidant (Sawaki *et al* 1981). In order to know whether there is any similarity in the reactivity and mechanism of permanganate ion oxidation of sulphides and sulphoxides, the kinetics of oxidation of several 4,4'-disubstituted diphenyl sulphoxides with permanganate ion has been studied spectrophotometrically and the results are reported here.

2. Experimental

Diphenyl sulphoxide and all 4,4'-disubstituted diphenyl sulphoxides have been synthesised by known procedures (Rheinboldt and Giesbrecht 1946; Leonard and Sutton 1948). Glacial acetic acid (BDH, Analar) has been purified by the method of Orton and Bradfield (1927). All sulphoxides were purified by distillation or recrystallisation before use and purity was checked by TLC and by recording IR spectra. All the other chemicals employed were of AR/GR grade or purified by known procedures. The kinetic studies were carried out spectrophotometrically under second-order conditions in 50% acetic acid–50% water (v/v) mixture. The reaction was followed by observing the decrease in optical density with time at 526 nm wavelength. All the kinetic runs were followed upto 80% completion of the reaction. The stoichiometry of the oxidation of DPSO to diphenyl sulphone has been found to follow the following reaction,

$$5(C_6H_5)_2SO + 2MnO_4^- + 6H^+ \rightarrow 5(C_6H_5)_2SO_2 + 2Mn^{2+} + 3H_2O. \quad (3)$$
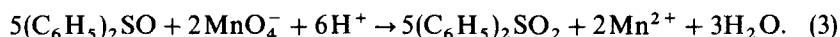
From this stoichiometric equation the expression for the second-order rate equation has been derived as

$$k_2 = \frac{2 \cdot 303}{t(a - 2 \cdot 5b)} \log \frac{b(a - 2 \cdot 5x)}{a(b - x)} \qquad (4)$$

where k_2, the second-order rate constant $(M^{-1}s^{-1})$, a, the initial concentration of the sulphoxide, b, the initial concentration of the permanganate, $(a - 2 \cdot 5x)$, the concentration of sulphoxide remaining after time t and $(b - x)$, the concentration of the permanganate remaining after time t seconds. The k_2 values have been evaluated from the slopes of the linear plots of $\log b(a - 2 \cdot 5x)/a(b - x)$ against t by the least squares method using a CASIO fx-3600P table calculator. The numerical value of k_2 has been obtained form the relation $k_2 = 2 \cdot 303 \times \text{slope}/(a - 2 \cdot 5b)$.

3. Results and discussion

The oxidation of diphenyl sulphoxide (DPSO) by permanganate ion is overall second order as shown by the linearity of plots of $\log b(a - 2.5x)/[a(b - x)]$ vs. time. The second order rate constant is independent of the initial concentration of DPSO and MnO_4^- (table 1), and hence the reaction is first order each in DPSO and MnO_4^-. Neither the change of $[H^+]$ nor ionic strength of the medium (I) has any influence on the rate of oxidation (table 2). The former observation rules out the participation of water molecule in the transition state and the latter points out that one of the reactants is a neutral species.

The influence of solvent on the rate of permanganate ion oxidation of DPSO has been studied by altering the composition of acetic acid of the medium. Though the rate constant decreases with the increase in the proportion of acetic acid (table 2), the change is not very significant and this is contrary to MnO_4^- oxidation of sulphides (Banerji 1988). The plot of $\log k_2$ against the inverse of dielectric constant is nonlinear. The observed solvent effect implies that a dipolar activated complex may be produced in the rate-limiting step but the polarisation is less compared to sulphide oxidation. Comparing sulphoxides with sulphides and sulphones, it has been well established that the latter are poorly solvated whereas sulphoxides are strongly solvated in

Table 1. Dependence of rate of reaction on $[MnO_4^-]$ and [DPSO] at 10°C.
Solvent: 50% (v/v) aqueous acetic acid; $I = 2 \times 10^{-4}M$

$10^4[MnO_4^-]$ (M)	$10^4[DPSO]$ (M)	k_2 (M^{-1}s^{-1})
2·0	6·0	9·05
2·0	7·0	9·90
2·0	7·5	9·21
2·0	8·0	9·29
2·0	8·5	9·00
2·0	9·0	9·16
2·0	10·0	9·21
2·6	9·0	9·59
3·0	9·0	9·39
3·5	9·0	9·21

Table 2. Dependence of the rate of oxidation on $[HClO_4]$, I and solvent composition. $[MnO_4^-] = 0.0002M$; [DPSO] $= 0.0009M$; $I = 2 \times 10^{-4}M$.

$[HClO_4]$ (M)	k_2 (M^{-1}s^{-1})	%H$_2$O − %HOAc (v/v)		k_2 (M^{-1}s^{-1})	I (M)	k_2 (M^{-1}s^{-1})
0.001	9·21	90	10	16·1	0·001	9·09
0·005	9·08	75	25	12·0	0·005	9·12
0·010	9·21	60	40	9·79	0·010	9·60
0·020	9·30	50	50	9·26		
0·050	9·60	20	80	8·64		
0·100	9·30	10	90	8·37		

proton-donating solvents (Curci and Edwards 1970). Hence, solvents which could solvate the sulphoxide should increase the rate of the first stage, $R_2S \rightarrow R_2SO$. On the other hand, the same solvents should decrease the rate of the second stage, $R_2SO \rightarrow R_2SO_2$. This fact has been confirmed from the results of Curci *et al* and others (Overberger and Cummins 1953; Curci *et al* 1968; Baliah and Satyanarayana 1978). Thus the observed solvent effect indicates that a mechanism different from sulphide oxidation is operating in the MnO_4^- oxidation of sulphoxides. However the increase in k value with the increase in water content of the medium indicates that an anion (MnO_4^-) and a neutral molecule are involved in the rate-determining step (Amis 1967).

3.1 *Substituent effect*

Owing to the ambient behaviour of sulphoxides, in oxidations, the study of the substituent effect and the sign of the reaction constant obtained from Hammett correlation indicate the nature of the behaviour of sulphoxide in this oxidation. To understand the mechanism of this reaction, kinetic studies have been carried out with several 4,4'-disubstituted diphenyl sulphoxides at three temperatures and the k_2 values are collected in table 3. The results clearly indicate that electron-withdrawing substituents accelerate the rate of oxidation. This behaviour is in sharp contrast to permanganate oxidation of organic sulphides (Banerji 1988). Hammett type correlations have been made with both σ and σ^+ (in figure 1, the plot of log k_2 vs. σ is given). In both cases, the correlations are fairly satisfactory but the correlation is better with σ rather than σ^+ ($\rho = 0.34$, $r = 0.950$, $n = 7$; $\rho^+ = 0.21$, $r = 0.911$, $n = 7$ at 30°C). The positive value of ρ indicates that a nucleophilic attack on the substrate is operating in this reaction. Thus this reaction is one of the rare examples where the mechanism of oxidation of organic sulphoxides differs from that of corresponding sulphides (Curci and Modena 1963, 1965, 1966; Curci *et al* 1966, 1977; Ogata and Suyama 1971; Sawaki *et al* 1981). The substituent effect observed in the permanganate oxidation of diaryl sulphoxides is also different from the behaviour of these sulphoxides with other oxidants. In the uncatalysed and picolinic acid-catalysed chromium (VI) oxidation of aryl methyl and diaryl sulphoxides, negative ρ values have been observed (Baliah and Satyanarayana 1978, 1980; Srinivasan *et al* 1981; Rajagopal 1984). Similar results

Table 3. Effect of substituents on the MnO_4^- oxidation of 4,4'-disubstituted diphenyl sulphoxides and activation parameters.

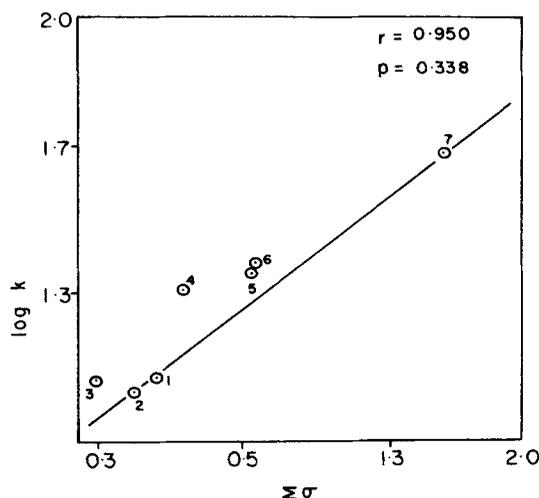|		$k_2(M^{-1}s^{-1})$			$\Delta H^{\neq}$	$-\Delta S^{\neq}$
No	Substituents at 4,4'-positions	10°C	20°C	30°C	(kJ mol^{-1})	(JK^{-1}mol^{-1})
1	H	9·26	10·2	11·5	5·30	207
2	CH$_3$	8·98	9·60	11·5	22·3	150
3	NHCOCH$_3$	8·16	9·48	10·9	15·3	183
4	F	15·2	17·3	19·9	7·22	196
5	Cl	16·7	18·8	22·0	7·31	195
6	Br	17·3	19·4	23·0	7·77	193
7	NO$_2$	19·2	28·8	44·0	27·4	123

Figure 1. Hammett plot of log k_2 vs. $\Sigma\sigma$ at 30°C. The points in the figure are referred to by the same numbers as the substituents in table 3.

have been observed in the co-oxidation of sulphoxides: Cr(VI): oxalic acid systems (Srinivasan *et al* 1987). Negative ρ values have also have been observed in the oxidation of aryl methyl and diaryl sulphoxides with several oxidants, for example in peroxomonosulphate (Suthakaran *et al* 1986), dimethyl oxirane (Murray *et al* 1987), chloramine T (Ganapathy and Jayagandhi 1978, 1983), bromamine T (Jegadeesan 1988), acid bromate (Srinivasan *et al* 1986), N-chlorophthalimide (Bhavani and Lily 1983) etc. However, positive ρ values have been reported only in three cases viz. in the oxidation of sulphoxides with peroxobenzoic acid and peroxides in alkaline medium (Curci and Modena 1963, 1965, 1966; Curci *et al* 1966, 1977; Ogata and Suyama 1971) and with fluorenone carbonyl oxides (Sawaki *et al* 1981).

3.2 *Mechanism of permanganate oxidation of diaryl sulphoxides*

Three types of mechanisms have been proposed so far for the oxidation of sulphoxides. Most of the reactions proceed by a mechanism involving rate-determining electrophilic attack of oxidant on the sulphur of the sulphoxide. However, single electron transfer mechanism in the rate-limiting step from the sulphoxide to the metal ion has been postulated in the Cr(VI) oxidation of sulphoxides (Baliah and Satyanarayana 1978, 1980; Srinivasan *et al* 1981) and cytochrome P-450 oxidation of substituted phenyl methyl sulphoxides (Watanabe *et al* 1982). On the other hand, in the alkaline peroxobenzoic acid and peroxide oxidation (Curci and Modena 1963, 1965, 1966; Curci *et al* 1966, 1977; Ogata and Suyama 1971) as well as in the fluorence carbonyl oxide oxidation of sulphoxides (Sawaki *et al* 1981), a nucleophilic attack of the oxidant on the sulphoxide in the rate-determining step has been suggested.

The study on the influence of substituents indicates that the behaviour of sulphoxides towards the permanganate ion is different from that of sulphides. Because of the difference in electronegativity between sulphur and oxygen, the S–O linkage in sulphoxide is in polarised form as S^+-O^-. Therefore a mechanism involving the

nucleophilic attack of MnO_4^- on the sulphur of the sulphoxide has been proposed as shown in scheme 1.
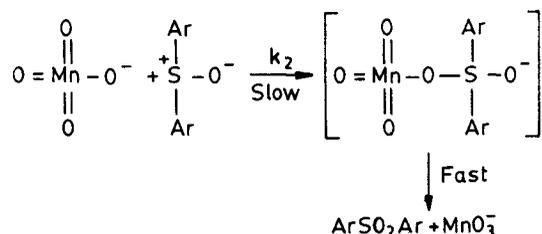
Scheme 1. Mechanism of MnO_4^- oxidation of diaryl sulphoxides.

The postulated mechanism resembles the one proposed by Curci and Modena (1963, 1965, 1966) and Curci et al (1966, 1977) for the alkaline peroxobenzoic acid and peroxide oxidation of sulphoxides wherein a positive ρ value has been obtained. A similar mechanism has also been envisaged in the base-catalysed oxidation of sulphoxides with organic hydroperoxide (Curci et al 1977). The observed ρ value of $+0.26$ in the fluorenone carbonyl oxide oxidation of substituted diphenyl sulphoxides (Sawaki et al 1981) is very close to the ρ value obtained in the present study ($\rho = +0.27$ at 20°C). Sawaki et al (1981) have proposed the following mechanism

$$R_2\overset{+}{C}OO^- + \overset{|}{S}=O \rightarrow R_2\overset{+}{C}OO\overset{|}{S}-\overset{-}{O} \rightarrow R_2C=O + \overset{|}{S}O_2. \qquad (6)$$
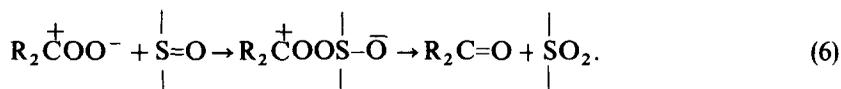
Thus the sign and magnitude of ρ value obtained in the present study point to a mechanism similar to the one proposed above. The one-electron transfer mechanism is ruled out as the rate is not affected when the reaction is carried out in the presence of vinyl monomer, acrylamide. Further, a better correlation of $\log k_2$ has been obtained with σ rather than σ^+. It is pertinent to mention here that in the cytochrome P-450 oxidation of sulphoxides wherein single electron transfer mechanism is proposed, the correlation is better with σ^+ than with σ (Watanabe et al 1982). The proposed mechanism is consistent with the following experimental observations:

(i) the reaction is first order with respect to MnO_4^- and DPSO,
(ii) electron-withdrawing groups accelerate the reaction whereas electron-releasing groups decelerate it, and
(iii) the increase of rate with increase in polarity of the medium. The absence of any influence of $[H^+]$ on the rate shows that the oxidant is MnO_4^- and not protonated before the reaction.

No definite conclusion can be derived from the thermodynamic parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$) presented in table 3. However, from the value of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ of the parent and substituted sulphoxides, the isokinetic temperature, β, has been evaluated from the isokinetic plot of $\Delta H^{\neq}$ vs. $\Delta S^{\neq}$ (Leffler and Grunwald 1963; Leffler 1955, 1966; Exner 1964). The isokinetic plot is linear ($r = 0.990$) and the value of β has been evaluated to be 280 K, close to the experimental temperature. Thus one of the reasons for the very low ρ value ($+0.12$) of the reaction at 10°C may be that the reaction has been carried out at a temperature close to the isokinetic temperature where the reaction is totally insensitive to variation in structure (Leffler 1966). It is pertinent to

point out here that in the permanganate oxidation of organic sulphides the value of isokinetic temperature has been reported as 454 K, much higher than the experimental temperature (Banerji 1988).

References

Amis E S 1967 *Solvent effects on reaction rates and mechanism* (New York: Academic Press)
Baliah V and Satyanarayana P V V 1978 *Indian J. Chem.* **A16** 966
Baliah V and Satyanarayana P V V 1980 *Indian J. Chem.* **B19** 620
Banerji K K 1988 *Tetrahedron* **44** 2929
Bhavani N and Lily 1983 *Curr. Sci.* **52** 872
Bordwell F G and Cooper G D 1952 *J. Am. Chem. Soc.* **74** 1058
Cerniani A and Modena G 1959 *Gazz. Chim. ital.* **89** 843
Curci R, Di Furia F and Modena G 1977 *J. Chem. Soc. Perkin Trans.* **2** 576
Curci R, Di Prete R, Edwards J O and Modena G 1968 *Hydrogen bonded Solvent Syst. Proc. Symp.* 1969 *Chem. Abstr.* **71** 48904r
Curci R and Edwards J O 1970 *Organic peroxides* (ed.) D Swern (New York: Interscience) p. 236
Curci R and Modena G 1963 *Tetrahedron Lett.* 1749
Curci R and Modena G 1965 *Tetrahedron Lett.* 863
Curci R and Modena G 1966 *Tetrahedron* **22** 1227
Curci R, Giovine A and Modena G 1966 *Tetrahedron* **22** 1235
Exner O 1964 *Collect. Czech. Chem. Comm.* **29** 1094
Ganapathy K and Jayagandhi P 1978 *Indian J. Chem.* **A16** 1978
Ganapathy K and Jayagandhi P 1978 *J. Indian Chem. Soc.* **55** 1074
Ganapathy K and Jayagandhi P 1983 *Int. J. Chem. Kinet.* **15** 129
Jegadeesan P P 1988 *Studies on substituent effects*, Ph D thesis, Madurai Kamaraj University
Leffler J E 1955 *J. Org. Chem.* **20** 1202
Leffler J E 1966 *J. Org. Chem.* **31** 533
Leffler J E and Grunwald E 1963 *Rates and equilibria of organic reactions* (New York: John Wiley)
Leonard N J and Sutton L S 1948 *J. Am. Chem. Soc.* **70** 1564
Murray L R, Jayaraman R and Krishna Pillay M 1987 *J. Org. Chem.* **52** 746
Ogata Y and Suyama S 1971 *Chem. Ind.* 707
Orton K J P and Bradfield A E 1927 *J. Chem. Soc.* 986
Overberger C G and Cummins R W 1953 *J. Am. Chem. Soc.* **75** 4783
Rajagopal S 1984 *Kinetics and mechanism of oxidation of organic compounds*, Ph D thesis, Madurai Kamaraj University
Rheinboldt H and Giesbrecht E 1946 *J. Am. Chem. Soc.* **68** 973
Sawaki Y, Kato H and Ogata Y 1981 *J. Am. Chem. Soc.* **103** 3832
Srinivasan C, Jegatheesan P P and Arumugam N 1986 *Indian J. Chem.* **A25** 678
Srinivasan C, Jegatheesan P P, Rajagopal S and Arumugam N 1987 *Can. J. Chem.* **65** 2421
Srinivasan C, Venkatasamy R and Rajagopal S 1981 *Indian J. Chem.* **A20** 505
Suthakaran R, Subramanian P and Srinivasan C 1986 *Proc. Indian Acad. Sci. (Chem. Sci.)* **97** 555
Watanabe Y, Takashi I and Oae S 1982 *Tetrahedron Lett.* 533