Mechanism of oxidation of aryl methyl sulfoxides with sodium hypochlorite catalyzed by (salen)Mn^{III} complexes

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Abstract

The oxidation of organic sulfoxides to sulfones with sodium hypochlorite catalyzed by (salen)Mn^{III} complexes in 90% acetonitrile–10% water (v/v) follows an overall second-order kinetics, first-order each in the oxo complex and the substrate. The less nucleophilic sulfoxides are more sensitive to substituent effect ($\rho = -2.57$) compared to the corresponding sulfides ($\rho = -1.85$). A positive ρ-value ($\rho = 0.50$) is observed in the oxidation of phenyl methyl sulfoxide by substituted oxo(salen)manganese(V) complexes. Substituent, acid and solvent effect studies reveal the operation of a common S_N2 mechanism. Correlation analyses establish that there is an inverse relationship between reactivity and selectivity in both the sulfoxide and complex series. A valid reactivity–selectivity principle (RSP) is observed in this redox system.

1. Introduction

Organic sulfides, which are strong nucleophiles, are oxidized to sulfoxides exclusively by electrophilic oxygen transfer reagents [1,2]. By contrast, sulfoxides are oxidized to sulfones by both electrophiles and nucleophiles [3–5]. With many oxidants it has been established that the ratio of reactivity, k_s/k_{so}, is very large and the nucleophilic reactivity of thioether is more affected by structural effects than that of sulfoxides [2,4–6]. We have initiated a systematic study on the oxygenation reactions of the organic sulfides and sulfoxides with oxometal complexes by taking Cr, Mn and Ru as metal ions. We have reported the mechanism of oxidation of organic sulfides [7–9] and sulfoxides [10] with PhIO catalyzed by (salen)Mn^{III} complexes and also the successful application of the reactivity–selectivity principle (RSP) to these oxidation reactions. The mechanistic studies of

oxo(salen)iron complexes [11,12] and oxo(salen)chromium(V) complexes [13,14] oxygenation reactions of organic sulfides and sulfoxides have been reported by Rajagopal and co-workers. Recently, we have published our results on the oxidation of organic sulfides with sodium hypochlorite catalyzed by (salen)Mn^{III} complexes [15]. A mechanism involving the electrophilic attack of the oxidant on the sulfide sulfur has been proposed [15]. A successful application of RSP to this oxidation has also been studied [16]. To understand whether the organic sulfoxides follow a mechanism similar to that of sulfides towards the oxidant oxo(salen)manganese(V) and the relevance of RSP in this redox system, we have studied spectrophotometrically the kinetics of oxidation of several aryl methyl sulfoxides with the six oxo(salen)manganese(V) complexes **2a–f** generated in situ from the corresponding [(salen)Mn^{III}]$^+$PF$_6^-$ complexes and NaOCl as represented in Eq. (1) and the results are analyzed here.

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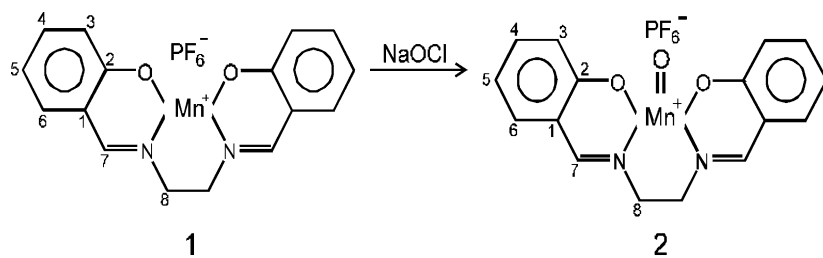
$$
\begin{array}{ll}
a & : \text{unsubstituted} \\
b & : 5,5'\text{-}(OCH_3)_2 \\
c & : 5,5'\text{-}Cl_2 \\
d & : 5,5'\text{-}(NO_2)_2 \\
e & : 7,7'\text{-}(CH_3)_2 \\
f & : 7,7'\text{-}Ph_2
\end{array}
$$

$$\tag{1}$$

2. Experimental

2.1. Materials

All the aryl methyl sulfoxides were prepared by known procedure [17]. The purity of sulfoxides was checked by ^{1}H NMR and HPLC analyses. Sodium hypochlorite (s.d. fine) was determined by an iodometric method. Doubly distilled water was used throughout, the second distillation being from permanganate. Acetonitrile (GR, E. Merck) was first refluxed over P_2O_5 for 5 h and then distilled. The $[(salen)Mn^{III}]^+PF_6^-$ complexes **1a–f** were synthesized according to reported procedure [10,18]. The results of IR and UV-visible spectral studies of all the complexes were found to be identical with literature data [18]. The oxo(salen)manganese(V) complexes **2a–f** were obtained by mixing equimolar quantities of complex and sodium hypochlorite. As the oxomanganese(V) complex undergoes auto-decomposition, the solutions were prepared freshly for each kinetic run.

2.2. Kinetic measurements

The kinetic studies were carried out in 90% acetonitrile–10% water (v/v) at $20 \pm 0.1\,^\circ$C under pseudo first-order conditions ([sulfoxide] > [oxo complex]) using a Perkin-Elmer UV–Vis spectrophotometer (Lambda 3B) fitted with thermostated cell compartments. Reaction mixtures for kinetic runs were prepared by quickly mixing the solutions of the oxo complex and sulfoxide in varying volumes so that in each run the total volume was 5 ml. The progress of the reaction was monitored by following the disappearance of oxomanganese(V) complex at 680 nm. The rate constants were computed from the linear least-square plots of $\log(A_t - A_\infty)$ versus time, where A_t is the absorbance at time 't' and A_∞ is the experimentally determined infinity point. The values of k_1 were obtained from $k_1 = k_{1(obs)} - k_{1(dec)}$, where $k_{1(dec)}$ represents the first-order rate constants for the auto-decomposition of oxo complex and $k_{1(obs)}$ represents the pseudo first-order rate constants for the decay of oxo complex in the

presence of sulfoxides. The second-order rate constants were obtained from $k_2 = k_1/[\text{sulfoxide}]$.

Gas chromatographic analyses of the samples showed that sulfone was the sole product. The reaction carried out under the experimental conditions ([**2a**] = 0.0026 M; [PhSOMe] = 0.20 M) gave sulfone in ca. 74% yield and $(salen)Mn^{III}$ complex in ca. 95% yield. Accordingly, the stoichiometry of the reaction can be represented by Eq. (2).

$$
O{=}Mn^V(salen)^+ + PhSOMe \rightarrow Mn^{III}(salen)^+ + PhSO_2Me
$$

$$\tag{2}$$
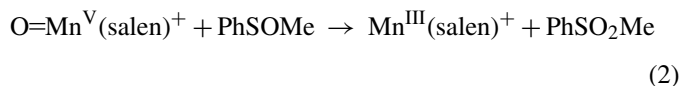
3. Results and discussion

3.1. Oxomanganese(V) species as the reactive intermediate

In the epoxidation of olefins with PhIO catalyzed by $(salen)Mn^{III}$ complexes, Kochi and co-workers [18] reported that the cationic $(salen)Mn^{III}$ complex readily reacts with PhIO to afford a new transient species, μ-oxomanganese(IV) dimer, $(salen)Mn^{IV}OMn^{IV}(salen)^{2+}$ and that the species itself cannot be the reactive intermediate which is directly responsible for oxygen atom transfer. They concluded that the reactive intermediate is the active oxomanganese(V) species capable of readily coupling with $(salen)Mn^{III}$ to afford the species μ-oxomanganese(IV) dimer (Eq. (3)). The μ-oxomanganese(IV) dimer disproportionates back to the active

$$
O{=}Mn^V(salen)^+ + (salen)Mn^{III}
$$
$$
\rightleftharpoons (salen)Mn^{IV}O^{IV}Mn(salen)^{2+}
$$

$$\tag{3}$$
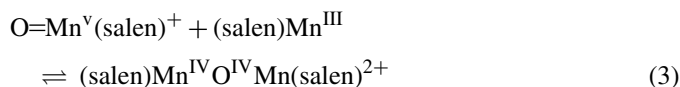
oxomanganese(V) (Eq. (3)) and serves as an alternate source of oxomanganese(V) ($\lambda_{max} \sim 530$ nm). Zhang and Jacobsen [19] and Katsuki [20] have proposed oxo(salen)manganese(V) as the active species in the $(salen)Mn^{III}$ catalyzed epoxidation of olefins with PhIO or NaOCl as suggested by Kochi in his original work [18]. Adam et al. [21,22] observed that the $(salen)Mn^V{=}O$ is the reactive intermediate in the $(salen)Mn^{III}$

catalyzed epoxidation of olefins with oxygen donors such as PhIO, NaOCl, C_6F_5IO, $TBAIO_4$ and O_3. In the (salen)Mn^{III} catalyzed epoxidation of *cis*-β-methylstyrene with NaOCl and *m*-chloroperbenzoic acid, Campbell et al. [23] reported the formation of (salen)Mn^{IV}=O and (salen)Mn^{III}OMn^{IV}(salen)$^+$ and shown that Mn^{IV} species is an inactive form of manganese-salen catalyst consistent with the observation made by Adam et al. [21]. Laser flash photolysis of a binuclear mixed valence complex Mn^{III}(salchd)OMn^{IV}(salchd)$^+$ leads to the formation of the reactive oxomanganese(V) complex [24] ($\lambda_{max} \sim 530$ nm), a species that has been proposed as key intermediate in the epoxidation reaction with manganese-salen system [18,22,25]. In a computational approach of the manganese-salen mediated alkene epoxidation, it is assumed that the reaction initiates from Mn^v=O species [26]. Further, in the recent report of Collman et al. [27] on the olefin epoxidation with ArIO catalyzed by (salen)Mn^{III} complexes, (salen)Mn^v=O species is shown to be the sole oxygenating intermediate. The active species in the present reaction is considered to be oxo(salen)manganese(V) complex, as proposed by Kochi and co-workers [18] and others [19–22,27] in the (salen)Mn^{III} catalyzed PhIO and NaOCl oxidation of achiral derivatives.

3.2. Oxidative conversion of manganese(III) to oxomanganese(V) species

The electronic spectra of clear brown solutions of (salen)Mn^{III} complexes in acetonitrile–water mixture are char-acterized by absorption bands with $\lambda_{max} \sim 350$ nm tailing to beyond 400 nm. When a clear brown solution of (salen)Mn^{III} is treated with equimolar quantities of sodium hypochlorite, it immediately turns dark brown, indicating the formation of oxo-manganese(V) species [15] ($\lambda_{max} \sim 530$ nm). The dark brown solution, on standing, faded to the original light brown within 2–3 h. When the same experiment was carried out in the presence of methyl phenyl sulfoxide (MPSO), the dark brown colour is discharged to original light brown within 40–50 min and methyl phenyl sulfone was isolated in 74% yield (Eq. (4)).

$$PhSOMe \xrightarrow[NaOCl]{(salen)Mn^{III}} PhSO_2Me \qquad (4)$$
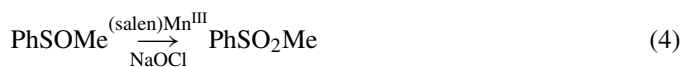
The absorption spectrum of the final solution coincided with that of the original (salen)Mn^{III} complex. As the isolation of pure oxo(salen)manganese(V) complexes is difficult [7–10,15,18], they were generated in situ for the studies reported here.

3.3. Kinetics of oxygen atom transfer from oxomanganese(V) to sulfoxides

The pseudo first-order rate constants (k_1) and second-order rate constants (k_2) at different [**2**]$_o$ and [MPSO]$_o$ are listed in Table 1. The reaction is first-order in **2a**, as evidenced from the linearity of $\log(A_t - A_\infty)$ versus time plots ($r > 0.995$), as well as from the constancy of k_1 values obtained upon varying [**2a**]$_o$ at constant [MPSO]$_o$ (Table 1). The k_1 value is sensitive to the change of [MPSO]$_o$ and varies linearly with [MPSO]$_o$ (Table 1).

Table 1
Rate constants for the oxidation of MPSO by **2a–f** in 90% acetonitrile–10% water (v/v) at 20 °C[a]

10^2[MPSO]$_o$ (M)	10^3[**2**]$_o$ (M)	$10^4 k_{1(obs)}$[b] (s^{-1})	$10^4 k_{1(dec)}$[c] (s^{-1})	$10^4 k_1$[d] (s^{-1})	$10^3 k_2$[e] (M^{-1} s^{-1})
	2a				
15.0	1.00	8.82 ± 0.16	5.44 ± 0.09	3.38 ± 0.07	2.25 ± 0.05
15.0	1.60	8.92 ± 0.25	5.72 ± 0.16	3.20 ± 0.09	2.13 ± 0.06
15.0	2.00	8.60 ± 0.09	5.24 ± 0.09	3.36 ± 0.00	2.24 ± 0.00
15.0	2.60	8.56 ± 0.19	5.52 ± 0.03	3.04 ± 0.16	2.03 ± 0.11
15.0	3.60	9.23 ± 0.14	5.99 ± 0.05	3.24 ± 0.09	2.16 ± 0.06
10.0	2.60	7.79 ± 0.18	5.52 ± 0.03	2.27 ± 0.15	2.27 ± 0.15
20.0	2.60	9.76 ± 0.17	5.52 ± 0.03	4.24 ± 0.14	2.12 ± 0.07
40.0	2.60	14.2 ± 0.2	5.52 ± 0.03	8.68 ± 0.17	2.17 ± 0.04
50.0	2.60	16.9 ± 0.4	5.52 ± 0.03	11.4 ± 0.4	2.28 ± 0.08
100.0	2.60	28.1 ± 0.7	5.52 ± 0.03	22.6 ± 0.7	2.26 ± 0.07
15.0[f]	2.60	8.19 ± 0.32	5.02 ± 0.10	3.17 ± 0.22	2.11 ± 0.15
15.0[g]	2.60	9.25 ± 0.14	5.89 ± 0.08	3.36 ± 0.06	2.24 ± 0.04
	2e				
10.0	2.60	7.24 ± 0.19	5.56 ± 0.06	1.68 ± 0.13	1.68 ± 0.13
100.0	2.60	23.8 ± 0.8	5.56 ± 0.06	18.2 ± 0.7	1.82 ± 0.07
	2f				
10.0	2.60	6.67 ± 0.24	5.29 ± 0.07	1.38 ± 0.17	1.38 ± 0.17
100.0	2.60	19.3 ± 0.9	5.29 ± 0.07	14.0 ± 0.8	1.40 ± 0.08

[a] As determined by a spectrophotometric technique following the disappearance of the oxo complex at 680 nm; the error quoted in k values is the 95% confidence limit of the Student's *t*-test [28].

[b] Estimated from pseudo first-order plots over 40% reaction.

[c] Estimated from first-order plots over 50–60% reaction in the absence of sulfoxide.

[d] Obtained as $k_1 = k_{1(obs)} - k_{1(dec)}$.

[e] Individual k_2 values estimated as k_1/[sulfoxide]$_o$.

[f] [PyO]$_o$ = 0.10 M.

[g] [PyO]$_o$ = 0.20 M.

Table 2
Effect of adding acid and changing the solvent composition on the rate of oxidation of MPSO by **2a** at 20 °C[a],[b]

10^3[acid] (M)	$10^4 k_1$[c] (s^{-1})	CH$_3$CN%–H$_2$O% (v/v)	$10^4 k_1$[d] (s^{-1})
0.0	2.27 ± 0.15	90–10	4.24 ± 0.14
0.5	2.80 ± 0.10	85–15	6.45 ± 0.09
1.0	3.90 ± 0.18	80–20	8.91 ± 0.13
5.0	12.1 ± 0.7	75–25	11.6 ± 0.2
10.0	22.8 ± 1.7	70–30	16.8 ± 0.5
20.0	54.4 ± 2.8		

[a] General condition: [**2a**]$_o$ = 0.0026 M.

[b] In the evaluation of rate constants, the self-decomposition of **2a** at different [acid] and solvent composition is taken into account.

[c] [MPSO]$_o$ = 0.10 M; solvent: 90% CH$_3$CN–10% H$_2$O (v/v).

[d] [MPSO]$_o$ = 0.20 M.

The second-order rate constants remain almost constant, indicating that the reaction is first-order with respect to MPSO. Also, that the first-order dependence on substrate is corroborated from the linear k_1 versus [MPSO]$_o$ plot which passes through origin ($r = 0.999$) and also from the unit slope obtained from the double logarithmic plot of k_1 versus [MPSO]$_o$ ($r = 0.998$). Similar kinetics were observed for the oxidation of substituted phenyl methyl sulfoxides with oxomanganese(V) complexes **2a–f**. Hence, the reaction follows an overall second-order kinetics, first-order each in oxo complex and sulfoxide and the rate law can be written as Eq. (5):

$$-\frac{d[\mathbf{2}]_o}{dt} = k_2[\mathbf{2}]_o[\text{sulfoxide}]_o \tag{5}$$

The reaction rate is unaffected by the addition of pyridine *N*-oxide (PyO) (Table 1). This demonstrates [29,30] that PyO is not binding with oxo(salen)manganese(V) complex and has no catalytic effect during the oxidation process. Similar results have been obtained in the epoxidation of olefins [18] and oxidation of aryl methyl sulfides [7,15] by oxo(salen)manganese(V) complexes. Kinetic studies at different concentrations of trichloroacetic acid and solvent compositions have been carried out and the rate data are collected in Table 2. The increase in concentration of acid, as well as the increase
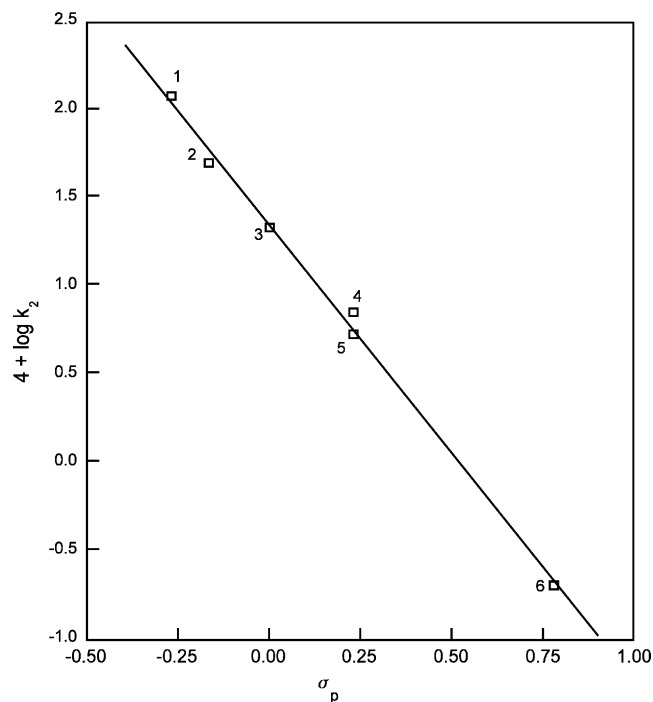
Fig. 1. Hammett plot for the oxidation of aryl methyl sulfoxides by **2a**. The points are referred to by the same numbers as in Table 3.

in the polarity of the medium enhance the rate of oxidation of MPSO.

The second-order rate constants for the oxidation of *para*-substituted phenyl methyl sulfoxides with oxo(salen)manganese(V) complexes **2a–d** are listed in Table 3. Electron-releasing substituents in the phenyl ring of PhSOMe enhance the rate while electron-withdrawing substituents retard the rate. The log k_2 values show better correlation with σ_p (Fig. 1, $r = 0.998$, $\rho = -2.57 \pm 0.09$, $s = 0.072$) rather than with σ^+/σ^- ($r = 0.981$, $\rho = -1.62 \pm 0.16$, $s = 0.212$). The negative reaction constant indicates an accumulation of positive charge at the sulfur centre, while the magnitude of ρ-value indicates the extent of charge development on the sulfur

Table 3
Second-order rate constants and ρ-values for the reactions of *p*-XC$_6$H$_4$SOMe with **2a–d** in 90% acetonitrile–10% water (v/v) at 20 °C[a]

No.	X	Oxo(salen)manganese(V) complex $10^3 k_2$ (M^{-1} s^{-1})				ρ[c]	(*r*)
		2b	**2a**	**2c**	**2d**		
1	OMe	8.65 ± 0.25	11.9 ± 0.6	15.7 ± 0.6	27.6 ± 1.1	0.240 ± 0.007	(0.999)
2	Me	3.51 ± 0.18	4.94 ± 0.18	7.30 ± 0.35	20.1 ± 0.9	0.367 ± 0.020	(0.997)
3	H	1.08 ± 0.08	2.12 ± 0.07	3.56 ± 0.17	12.3 ± 0.5	0.500 ± 0.005	(0.999)
4	Cl	0.38 ± 0.06	0.71 ± 0.10	1.53 ± 0.04	5.35 ± 0.30	0.554 ± 0.027	(0.998)
5	Br	0.25 ± 0.07	0.53 ± 0.05	1.28 ± 0.12	3.87 ± 0.30	0.576 ± 0.057	(0.990)
6	NO$_2$[b]	0.01 ± 0.00	0.02 ± 0.01	0.06 ± 0.02	0.23 ± 0.05	0.661 ± 0.060	(0.992)
	ρ[d]	−2.74 ± 0.01	−2.57 ± 0.09	−2.23 ± 0.10	−1.98 ± 0.15		
	(*r*)	(0.997)	(0.998)	(0.996)	(0.990)		

[a] General conditions: [**2**]$_o$ = 0.0026 M; [sulfoxide]$_o$ = 0.20 M.

[b] [sulfoxide]$_o$ = 0.50 M.

[c] The values were obtained by correlating log k_2 with $2\sigma_p$ for the reaction of various oxo(salen)manganese(V) complexes with a given sulfoxide.

[d] The values were obtained by correlating log k_2 with σ_p for the reaction of various sulfoxides with a given oxo(salen)manganese(V) complex.
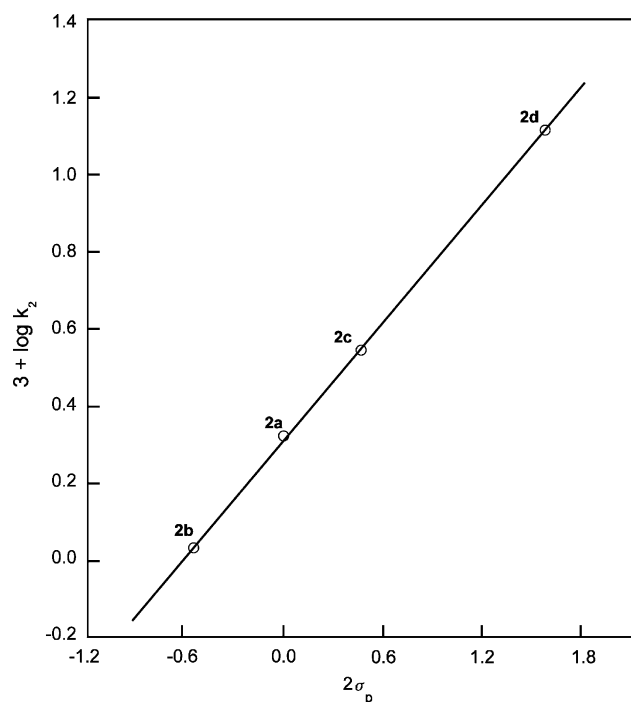
Fig. 2. Hammett plot for the oxidation of MPSO by substituted oxo(salen)-manganese(V) complexes.

atom in the transition state of the rate-determining step [31]. Electron-withdrawing substituents at the 5,5′-positions of the salen ligand accelerate the rate, whereas electron-releasing substituents decelerate it. Hammett correlation of $\log k_2$ versus $2\sigma_p$ shows an excellent linear relationship with $\rho = 0.50 \pm 0.01$ (Fig. 2, $r = 0.999$, $s = 0.012$). It is interesting to compare the present results with those observed for the oxidation of organic sulfides (Table 4) [15,16]. The electronic effect is more pronounced with sulfoxide oxidation and the ρ-value is uniformly higher with sulfoxides. The effect of substituents at the 7,7′-positions of salen ligand of oxo(salen)manganese(V) complexes on the reaction rate was studied using **2a**, **2e** and **2f** for the oxidation of phenyl methyl sulfoxide. The rate data in Table 1 show that the presence of methyl or phenyl group at the

7,7′-positions slightly reduces the rate, as in the case of sulfide oxidation [15].

3.4. Mechanism of the oxygen atom transfer from oxomanganese(V) to sulfoxides

Three types of mechanisms viz.: (i) a rate-determining electrophilic attack of the oxidant on the sulfur of the sulfoxide [10,32–36]; (ii) a single electron transfer from the sulfoxide to the metal ion in the rate-limiting step [37–39]; and (iii) a nucleophilic attack of the oxidant on the sulfoxide in the rate-determining step [3,40,41], have been reported so far for the oxygenation of organic sulfoxides. In the present investigation, let us consider how the oxygen atom is actually transferred from the oxo species to the sulfoxide in the rate-limiting step. The observed overall second-order kinetics, first-order each in oxo(salen)manganese(V) complex and sulfoxide indicate that the oxidation mechanism is a simple bimolecular process not involving coordination of the substrate to the metal. Substituent effect studies can give an insight into the mechanism of $[(salen)Mn^V=O]^+$ oxidation of organic sulfoxides. The observed ρ-value of -2.57 ± 0.09 is close to the ρ-values found for the oxidation of substituted phenyl methyl sulfoxides by potassium bromate [32] ($\rho = -2.05$) and by chloramine-T [33] ($\rho = -2.02$). These reactions were characterized as proceeding through an electrophilic attack by a halogen ion on the sulfur centre of the sulfoxide in the rate-determining step. In the Lewis acid catalyzed permanganate oxidation of sulfoxides [42] ($\rho = -2.18$), nucleophilic attack of sulfur atom on the metal centre or on the oxygen atom of the permanganate ion has been proposed. However, in the oxidation of phenyl methyl sulfoxides by dioxiranes [34] ($\rho = -0.76$), gem-dialkylperoxonium ion [35] ($\rho = -0.83$), Cr(VI)-oxalic acid [36] ($\rho = -0.93$), methyltrioxorhenium(VII) catalyzed H_2O_2 [43] ($\rho = -0.65$), and oxo(phosphine)ruthenium(IV) complexes [44] ($\rho = -0.42$), although low ρ-values have been observed, an S_N2 mechanism has been postulated. In the present study, since the observed ρ-value is high, similar to the ρ-value (-2.44) observed for PhIO oxidation of sulfoxides catalyzed by (salen)Mn^III^ complexes [10] and $\log k_2$ values are better correlated with σ_p than

Table 4
Second-order rate constants and ρ-values for the reactions of p-XC_6H_4SMe with **2a**–**d** in 90% acetonitrile–10% water (v/v) at 20 °C[a]

X	Oxo(salen)manganese(V) complex $10^3 k_2$ (M^{-1}s^{-1})				ρ	(r)
	2b	**2a**	**2c**	**2d**		
OMe	14.3 ± 0.6	16.5 ± 0.7	23.1 ± 0.8	35.3 ± 1.3	0.193 ± 0.018	(0.991)
Me	6.05 ± 0.15	10.2 ± 0.4	14.6 ± 0.5	28.8 ± 1.3	0.317 ± 0.025	(0.994)
H	2.91 ± 0.13	4.29 ± 014	9.20 ± 0.25	26.8 ± 1.1	0.476 ± 0.038	(0.994)
F	2.19 ± 0.04	3.64 ± 0.19	7.90 ± 0.25	21.4 ± 0.6	0.480 ± 0.041	(0.993)
Cl	1.17 ± 0.04	2.03 ± 0.06	4.31 ± 0.22	12.8 ± 0.4	0.502 ± 0.031	(0.996)
Br	0.98 ± 0.04	1.66 ± 0.09	3.91 ± 0.22	11.1 ± 0.3	0.515 ± 0.046	(0.992)
COOH	0.48 ± 0.04	0.76 ± 0.08	2.79 ± 0.18	7.03 ± 0.36	0.581 ± 0.103	(0.970)
COMe	0.26 ± 0.04	0.55 ± 0.08	1.71 ± 0.08	4.17 ± 0.23	0.583 ± 0.094	(0.975)
NO$_2$	0.09 ± 0.02	0.18 ± 0.04	0.53 ± 0.04	1.84 ± 0.09	0.634 ± 0.062	(0.991)
ρ	-2.02 ± 0.08	-1.85 ± 0.04	-1.47 ± 0.08	-1.25 ± 0.10		
(r)	(0.995)	(0.998)	(0.991)	(0.978)		

[a] Data taken from ref. [16].

Scheme 1. Mechanism of [(salen)Mn^V=O]$^+$ oxidation of organic sulfoxides.

σ^+/σ^+, one may anticipate an S_N2 mechanism involving the rate-determining electrophilic attack of the oxidant on the sulfur of the sulfoxide. The positive ρ-value of 0.50 ± 0.01 obtained from the Hammett correlation of $\log k_2$ versus $2\sigma_p$ (Fig. 2) indicates the build-up of negative charge on the metal centre in the transition state of the rate-determining step, as would be expected in the reduction of manganese(V) to manganese(III). It is pertinent to mention here that the ρ-values of 0.37 and 0.52 have been reported, respectively, for the oxidation of methyl phenyl sulfoxide with substituted oxo(phosphine)ruthenium(IV) [44] and (salen)Mn^{III} complexes catalyzed PhIO [10], where an S_N2 mechanism has been proposed.

A clear picture of the mechanism of this reaction may emerge by comparing the present results with those observed for the (salen)Mn^{III} catalyzed NaOCl oxidation of organic sulfides (Table 4) [15,16]. In many reactions [12,14,45–47], the comparison of ρ-values points out that the values for thioether oxidation are consistently larger than those of sulfoxides. However, the reactivity of organic sulfides and sulfoxides towards oxomanganese(V) complexes is comparable and the ρ-values are higher with sulfoxides (Tables 3 and 4). Sulfoxides react faster than sulfides with the same oxidant only if the sulfoxide behaves as an electrophile rather than a nucleophile and ρ-value becomes positive [3,40,41]. As the ρ-value observed in the present study is negative (−2.57), the sulfoxides behave only as strong nucleophiles. These results may be taken as evidence for the operation of an S_N2 mechanism for the oxidation of organic sulfoxides. The observed acid and solvent effects (Table 2) are very similar to those observed in the sulfide oxidation [15] where an S_N2 mechanism operates.

Based on the above arguments, the following S_N2 mechanism is proposed for the oxidation of aryl methyl sulfoxides by oxo(salen)manganese(V) complexes (Scheme 1). The proposed mechanism envisages the formation of intermediate I in the rate-limiting electrophilic attack of the oxo complex on the sulfoxide, which then decomposes to give (salen)Mn^{III} and sul-

fone as the products. The observed small steric effect when bulky methyl or phenyl group present in 7,7′-positions (Table 1) of the salen ligand excludes the possibility of oxametallacyclic intermediate [48]. Although less nucleophilic sulfoxides are more sensitive to substituent effect, the k_2 values obtained for sulfides (Table 4) are always two to three times more than the k_2 values observed for the corresponding sulfoxides (Table 3). These data are in accordance with the Hammond postulate, i.e. consistent with a common S_N2 mechanism wherein only the position of the transition state changes from one substrate class to the next. The more electron-rich sulfides should have an earlier transition state for interaction with an electrophilic metal oxo complex and will thus exhibit less charge on S and a weaker influence of the substituent, leading to a low ρ-value. The reverse is the case with less nucleophilic sulfoxides giving a comparitively higher ρ-value. The excellent linear correlation shown by $\log k_2$ of aryl methyl sulfoxides with $\log k_2$ of aryl methyl sulfides ($r = 0.998$, slope $= 1.39 \pm 0.05$, $s = 0.066$) also suggests a similar mechanism for the oxidation of these two substrates. It is pertinent to mention here that, in the oxo(salen)iron oxidation of organic sulfoxides [12], a direct oxygen transfer from the oxidant to the substrate has been postulated and in the oxo(salen)chromium(V) oxidation of organic sulfoxides [14], a mechanism involving a bimolecular electrophilic oxidation performed by oxidant-sulfoxide adduct at non-ligated sulfoxide has been proposed.

3.5. Reactivity–selectivity principle

The last row of Table 3 contains ρ-values for substituent variation in sulfoxides for each oxo(salen)manganese(V) complex, while the last column shows ρ-values for substituent variation in oxo(salen)manganese(V) complex for each sulfoxide. An analysis of the ρ-values establishes the inverse relationship between reactivity and selectivity both in the sulfoxide and in the oxo(salen)manganese(V) complex as shown by the significant increase in ρ-values with decreasing reactivity of either sulfoxide or oxo(salen)manganese(V) complex. Similar to earlier studies [8–10,13,16], the rate data in Table 3 were subjected to Exner's mathematical treatment as per Eqs. (6) and (7) [49]:

$$\log k_{Fi} = a + b \log k_{Si} + \varepsilon_i \qquad (6)$$

$$\Delta = \frac{\sum \log k_{Fi} - \sum \log k_{Si}}{N} \qquad (7)$$

where k_{Fi} and k_{Si} are the second-order rate constants for the reactions of fast and slow reagents (oxo complexes), respectively, with each sulfoxide and ε_i is the error of the $\log k_{Fi}$ versus

Table 5
Results of correlation between $\log k_{Fi}$ and $\log k_{Si}$ according to Eq. (6) for aryl methyl sulfoxides[a]

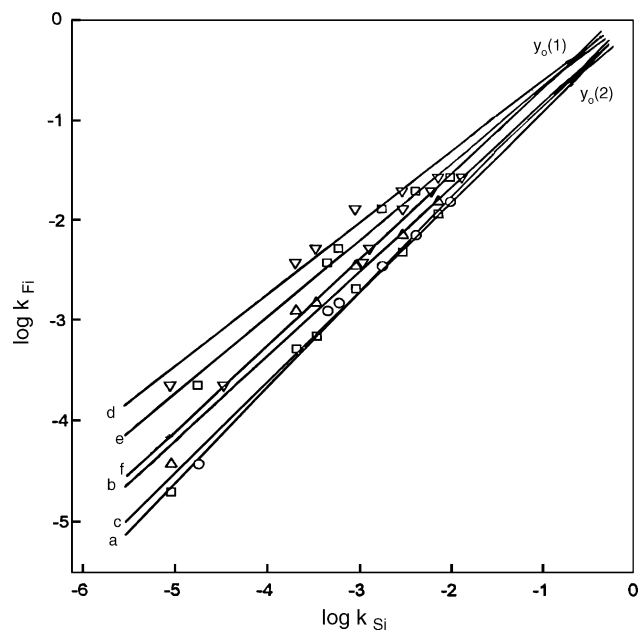| Results	Oxo(salen)manganese(V) complexes (F&S)					
	2a and 2b	2c and 2b	2c and 2a	2d and 2b	2d and 2a	2d and 2c
r	0.998	0.995	0.999	0.985	0.992	0.994
b	0.938 ± 0.028	0.810 ± 0.039	0.866 ± 0.020	0.720 ± 0.066	0.772 ± 0.052	0.892 ± 0.054
Δ	0.250	0.533	0.283	1.00	0.756	0.468

[a] $[2]_o = 0.0026$ M.

Fig. 3. Log k_{Fi} vs. log k_{Si} plots for the reactions of aryl methyl sulfoxides with: (a) **2a** and **2b**; (b) **2c** and **2b**; (c) **2c** and **2a**; (d) **2d** and **2b**; (e) **2d** and **2a**; and (f) **2d** and **2c**.

log k_{Si} correlation and Δ the mean difference. The values of b and Δ were calculated for all the six possible combinations of one fast and one slow reagent (among the four oxo complexes) with a series of similar substrates (six sulfoxides). The results summarized in Table 5 show a valid RSP in all cases as the value of b is less than unity and Δ is not too small.

In a reaction series involving more than one reagent and the same set of substrates, the existence of a 'magic point' [49] in the log k_{Fi} versus log k_{Si} plots is an indication for a strong RSP. The magic point represents some limiting value of reactivity in which, for a particular substrate, the reaction rate is independent of the reagent and vice versa. In this aspect, the present system reveals interesting results (Fig. 3). The correlations involving nitro-substituted oxo complex **2d** (lines d–f) produce one magic point, $y_o(1)$ and the correlations involving other oxo complexes (lines a–c) produce another magic point, $y_o(2)$. Both the magic points are situated on the side of high reactivity, as expected for a valid RSP [8–10,12,13,16,49–51]. These results are very similar to those observed with aryl methyl sulfides [15]. The success of RSP reveals the operation of a common mechanism for the oxidation of all organic sulfides and sulfoxides.

4. Conclusion

Oxo(salen)manganese(V) complexes oxidize aryl methyl sulfoxides to sulfones. The mechanism of this oxidation has been elucidated by varying the electronic nature of the substrates and oxidants. The less nucleophilic sulfoxides are more sensitive to substituent effect ($\rho = -2.57$) compared to the corresponding sulfides ($\rho = -1.85$). A common mechanism involving direct oxygen transfer from the oxidant to substrate has been proposed for the oxidation of organic sulfides and sulfoxides with sodium

hypochlorite catalyzed by (salen)Mn^{III} complexes. The operation of a valid RSP has been established in this redox system.

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