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Kinetics and mechanism of oxidation of aryl methyl sulfoxides with (salen)Mn^{III}/H_2O_2 catalytic system

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ABSTRACT

The kinetics of (salen)Mn^{III} complexes-catalysed oxidation of aryl methyl sulfoxides with hydrogen peroxide in 80% acetonitrile–20% water solvent mixture at 25 °C has been followed spectrophotometrically. The reaction is first-order in (salen)Mn^{III}, zero-order in hydrogen peroxide and fractional-order in sulfoxide. Also, it has been found that nitrogenous bases affect the oxidation, while free-radical inhibitor does not. However, an increase in the water content of the solvent mixture causes an increase in the rate of reaction. Stoichiometry between H_2O_2 and sulfoxide has been found to be 1:1 and the product analysis confirms the formation of sulfone and the regeneration of (salen)Mn^{III} complex. These observations have been well analyzed in favor of a Michaelis–Menten type mechanism, involving a manganese(III)–hydroperoxide complex as the reactive species. Using the derived rate law, the oxidant–substrate complex formation constant, K and the oxidant–substrate complex decomposition rate constant, k_2 have been evaluated. The proposed mechanism has been well supported by electronic-oxidant and electronic-substrate effect studies.

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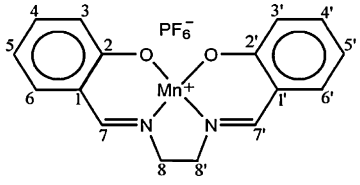
1. Introduction

Transition metal complexes of porphyrin [1–5], Schiff-base [6–19] and pthalocyanin [20] ligands have widely been explored in the past decades as catalysts in the reactions of oxygen atom transfer from terminal oxidants to organic substrates. The activity of these complexes varied with the nature of ligands, coordination sites, metal ions and the terminal oxidants. During the past years, we are investigating on the catalytic efficiency of (salen)M^{III} complexes (salen = N,N′-ethylenebis(salicylideneaminato) and M = Mn, Cr, or Ru) in oxidising organic sulfides and sulfoxides with PhIO, H_2O_2 and NaOCl as terminal oxidants [21–31]. Among the various terminal oxidants, hydrogen peroxide has the distinction of being designated as 'green reagent' because of its non-toxic side-product, water and its cheap availability. In reactions involving hydrogen peroxide and alkyl hydroperoxides [5,6,32,33], the metal complexes have been shown to be effective in activating the peroxide group and minimizing the importance of free-radical pathways, thus making the reactions proceed faster with less-complicated mechanisms. Recently we have reported [29] that the (salen)Mn^{III}-catalysed hydrogen peroxide oxidation of alkyl aryl sulfides proceeds by a Michaelis–Menten type mechanism. Organic sulfoxides may behave as electrophiles as well as nucleophiles, depending on the nature of the oxidant [34–37]. Keeping this biphilic nature of sulfoxides in mind, we extended our study to sulfoxides also with a view to compare the behaviors of sulfides and sulfoxides towards (salen)Mn^{III}/H_2O_2 catalytic system. Hereunder, we report the results of a detailed kinetic study on the oxidation of several aryl methyl sulfoxides with H_2O_2 catalysed by (salen)Mn^{III} complexes, **1a**–**f**.



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a: $[(5,5'-H_2Salen)Mn^{III}]^+PF_6^-$

b: $[(5,5'-(OMe)_2Salen)Mn^{III}]^+PF_6^-$

c: $[(5,5'-Cl_2Salen)Mn^{III}]^+PF_6^-$

d: $[(5,5'-(NO_2)_2Salen)Mn^{III}]^+PF_6^-$

e: $[(7,7'-Me_2Salen)Mn^{III}]^+PF_6^-$

f: $[(7,7'-Ph_2Salen)Mn^{III}]^+PF_6^-$

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2. Experimental

2.1. Materials

All the aryl methyl sulfoxides were prepared by known methods [38]. The purity of sulfoxides was checked by ^{1}H NMR ad HPLC analyses. (Salen)Mn^{III} complexes **1a**–**f** were synthesized by the reported method [21]. The results of IR and UV–vis spectral studies of all the complexes were found to be identical with the literature data [10]. Acetonitrile (GR, E. Merck India) was first refluxed over P_2O_5 for 5 h and then distilled. EPR spectra were recorded with a JEOL JES-TE 100 X-band EPR spectrometer in CH_3CN.

2.2. Kinetic measurements

The kinetic runs of the oxidation of aryl methyl, alkyl phenyl sulfides with hydrogen peroxide in the presence of **1a**–**f** were conducted in 80% acetonitrile–20% water at 25 ± 0.1 °C under pseudo-first-order conditions using 10–100-fold excess of sulfide over H_2O_2. Reaction mixtures for the kinetic runs were prepared by mixing the standard solutions of (salen)Mn^{III}, sulfoxide and H_2O_2 in varying volumes so that in each run the total volume did not exceed 5.0 ml. The reaction mixture was shaken well and quickly transferred to the 1 cm quartz cuvette. The progress of the reaction was monitored by following the changes in absorbance values at 400 nm in a PerkinElmer UV–vis spectrophotometer (Lambda 3B) fitted with thermostated cell compartments. At higher complex concentrations the reactions were followed at higher wavelengths in order to keep the absorbance values in a reliable range.

The pseudo-first-order rate constants (k_{obs}) for the initial 15–20% of the reaction were estimated from the slopes of linear least square plots of $\ln(A_t - A_\infty)$ versus time, where A_t is the absorbance at time t and A_∞ is the experimentally determined infinity point. The precision of k_{obs} values is given in terms of 95% confidence limit of 'Student's t' test [39]. The oxidant–substrate complex decomposition rate constant (k_2) and the complex formation constant (K) were then obtained from the slope and intercept of double reciprocal plot of k_{obs} versus $[\text{sulfoxide}]_o$.

2.3. Stoichiometry and product analysis

To a solution of **1a** (0.0004 M) and methyl phenyl sulfoxide (MPSO) (0.01 M) in acetonitrile was added an aqueous solution of H_2O_2 (0.0004 M) and the composition of acetonitrile and water in the solvent mixture was maintained at 80:20 by adding the solvents in the required proportions at 25 °C under nitrogen atmosphere. The reaction gave methyl phenyl sulfone in ~85% yield with negligible amount of sulfone, which established a 1:1 stoichiometry between MPSO and H_2O_2 as represented by Eq. (1):

$$H_2O_2 + \text{ArSOMe} \xrightarrow{\text{(salen)Mn}^{III}} \text{ArSO}_2\text{Me} + H_2O \quad (1)$$

Product analyses were done using a Shimadzu LC-8A modular HPLC system (reverse phase column (ODS), UV-detector at 258 nm) using 70% methanol as the mobile phase. A mixture of **1a** (0.0006 M), MPSO (0.08 M) and H_2O_2 (0.006 M) in 80% acetonitrile–20% water was allowed to stand overnight. The reaction mixture was extracted with chloroform and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. GC and TLC analyses of the residue showed the product to be methyl phenyl sulfone (~85%). After the organic product was chloroform extracted the left behind brown residue gave an absorption spectrum which resembled that of (salen)Mn^{III} complex. The product analyses carried out with other complexes and other sulfoxides also showed the formation of corresponding sulfone as the product. The percentage yields of sulfones determined from HPLC analyses ranged between 70 and 90 depending on the complex and the sulfoxide employed.

3. Results and discussion

3.1. Identification of the reactive species

When an aqueous solution of H_2O_2 (0.04 mol dm^{-3}) is added to a clear brown solution of **1a** (0.0004 mol dm^{-3}; λ_{max} ~350 nm) at 25 °C, the solution gets darkened (λ_{max} shifts to ~420 nm) with a brisk evolution of dioxygen as represented in Eq. (2):

$$H_2O_2 \rightarrow 2H_2O + O_2 \quad (2)$$

This establishes the catalase-like activity of (salen)Mn^{III} complexes as reported for the other mono- and di-nuclear manganese, iron and cobalt complexes in acetonitrile [40–43]. Nitrogenous bases such as 1-methylimidazole, 2-methylimidazole and pyridine accelerate the dismutation of H_2O_2 as indicated by the more vigorous evolution of oxygen, thus increasing the catalase-like activity of **1a**–**f** by binding to the metal centre [5]. Addition of MPSO to the solution greatly diminishes oxygen evolution and the UV–vis spectral analysis of the solution shows a progressive shifting of λ_{max} from ~420 nm back to ~350 nm. The catalyst-like nature of the complex is evident from the fact that same changes are observed on addition of fresh quantities of H_2O_2 and MPSO. However, the complex gets decomposed to unknown products (the brown colour of the solution gets bleached) after few (10–12) additions. Thus it is clear that mixing the solutions of **1a** and H_2O_2 produces a reactive species (λ_{max} ~420 nm) which is responsible for the catalase-like activity as well as for the oxidation of sulfoxides. Another interesting observation is that when MPSO is added to the mixture of **1a** and H_2O_2 in the presence of a nitrogenous base, 1-methylimidazole, 2-methylimidazole or pyridine, oxygen evolution is not diminished, indicating that oxidation of MPSO does not start. This shows that the nitrogenous bases have strong binding affinity for the metal centre of the reactive species than MPSO, and binding of sulfoxide to the reactive species is an essential condition for the oxidation reaction to proceed.

Based on UV–vis and EPR spectral studies and analysis of literature, we have clearly established (for a detailed discussion, *see* Ref. [29]) that this reactive species is a low-spin, EPR inactive Mn^{III}–hydroperoxide complex, [(salen)Mn^{III}OOH], the formation of which is represented as:

$$[(\text{salen})\text{Mn}^{III}]^+ + H_2O_2 + H_2O \rightarrow \underset{(C_1)}{[(\text{salen})\text{Mn}^{III}\text{OOH}]} + H_3O^+ \quad (3)$$

The kinetics of oxidation of aryl methyl sulfoxides was carried out under such [complex] to [H_2O_2] ratios (between 1:30 and 1:10) that the dismutation of H_2O_2 was insignificant (as evidenced by the iodometric estimation of residual hydrogen peroxide) and only the oxidation of sulfoxide proceeded.

3.2. Kinetics of oxidation of aryl methyl sulfoxides

The kinetics of oxidation of aryl methyl sulfoxides by H_2O_2 in presence of (salen)Mn^{III} complexes, **1a**–**f**, in 80% acetonitrile–20% water at 25 °C were monitored by following the absorbance changes at 400 nm. The pseudo-first-order rate constants (k_{obs}) obtained for the oxidation of MPSO catalysed by **1a**–**f** are listed in Tables 1 and 2. Comparison of the first two entries in Table 1 shows that the catalysed oxidation of MPSO is ~40 times faster than the uncatalysed reaction. Hence the contribution of uncatalysed reaction between MPSO and H_2O_2 can be neglected. Furthermore, if sulfoxide is added sometime after mixing H_2O_2 and complex, the rate constants are lower than those obtained when sulfoxide is added immediately by only 5–10% depending on the length of

Table 1
Pseudo-first-order rate constants for the oxidation of MPSO with H_2O_2 catalysed by **1a** at 25 °C in 80% acetonitrile–20% water[a].

10^2[MPSO] (M)	10^3[H_2O_2] (M)	10^4[**1a**]$_o$ (M)	$10^4 k_{obs}$ (s^{-1})
15.0	10.0	–	0.09 ± 0.02[b]
15.0	10.0	10.0	3.51 ± 0.07[b]
8.0	6.0	2.0	0.96 ± 0.03
8.0	6.0	3.0	1.05 ± 0.03
8.0	6.0	4.0	1.06 ± 0.02
8.0	6.0	5.0	1.05 ± 0.03
8.0	6.0	6.0	0.95 ± 0.03
8.0	2.0	2.0	1.00 ± 0.02
8.0	3.0	2.0	0.99 ± 0.03
8.0	4.0	2.0	1.08 ± 0.01
8.0	5.0	2.0	1.05 ± 0.02
8.0	7.0	2.0	1.04 ± 0.02

[a] The k_{obs} values were determined by a spectrophotometric technique following the absorbance changes at 400 nm over 15–20% of reaction; the error quoted in k_{obs} values is 95% confidence limit of 'Student's *t*' test.
[b] Estimated iodometrically by following the unreacted H_2O_2.

Table 2
Pseudo-first-order rate constants for the oxidation of MPSO with H_2O_2 catalysed by **1b–f** at 25 °C in 80% acetonitrile–20% water[a].

[MPSO]$_o$ (M)	Complex $10^4 k_{obs}$ (s^{-1})					
	1a	**1b**	**1c**	**1d**	**1e**	**1f**
0.04	0.77 ± 0.01	0.62 ± 0.01	1.14 ± 0.03	2.90 ± 0.07	0.57 ± 0.01	0.43 ± 0.01
0.08	1.04 ± 0.02	0.84 ± 0.01	1.54 ± 0.05	3.89 ± 0.06	0.78 ± 0.01	0.58 ± 0.01
0.15	1.26 ± 0.01	1.00 ± 0.02	1.94 ± 0.04	4.78 ± 0.09	1.01 ± 0.03	0.82 ± 0.01
0.30	1.51 ± 0.92	1.25 ± 0.02	2.36 ± 0.05	5.75 ± 0.09	1.24 ± 0.04	1.01 ± 0.01
0.40	1.63 ± 0.03	1.31 ± 0.03	2.55 ± 0.04	6.05 ± 0.12	1.30 ± 0.03	1.05 ± 0.02
Order in MPSO[b]	0.32	0.32	0.35	0.32	0.36	0.40

[a] General conditions: [complex]$_o$ = 0.0004 M; [H_2O_2]$_o$ = 0.004 M.
[b] Slope values of double logarithmic plots of k_{obs} versus [MPSO]$_o$.

the interval period. Therefore, the self-decay of the complex in the absence of sulfoxide seems not to be substantial.

Analysis of rate data in Table 1 points out that changes in the initial concentration of complex do not have any influence on reaction rate. This, coupled with the excellent linearity ($r > 0.990$) observed in $\ln(A_t - A_\infty)$ versus time plots ensures the order of the reaction with respect to complex is one. Also, the constant k_{obs} values at different initial concentration of H_2O_2 indicate that the reaction is zero-order with respect to H_2O_2. The k_{obs} values measured at different initial concentrations of MPSO for reactions catalysed by **1a–f** (Table 2) do not increase linearly with increasing concentration of sulfoxide and saturation kinetics is observed at higher substrate concentrations. The fractional-order dependence on [MPSO]$_o$ is further evidenced from the fractional slopes (Table 2) shown by the double logarithmic plots between k_{obs} and [sulfoxide]$_o$ ($r > 0.990$). It can be understood from the direct plots of k_{obs} versus [sulfoxide]$_o$ (Fig. 1) that saturation kinetics is observed with other aryl methyl sulfoxides also, establishing that the reaction follows Michaelis–Menten type kinetics involving an intermediate complex formation between the oxidant and the sulfoxide. The influence of nitrogenous bases on the reaction (Section 3.1) also upholds this finding.

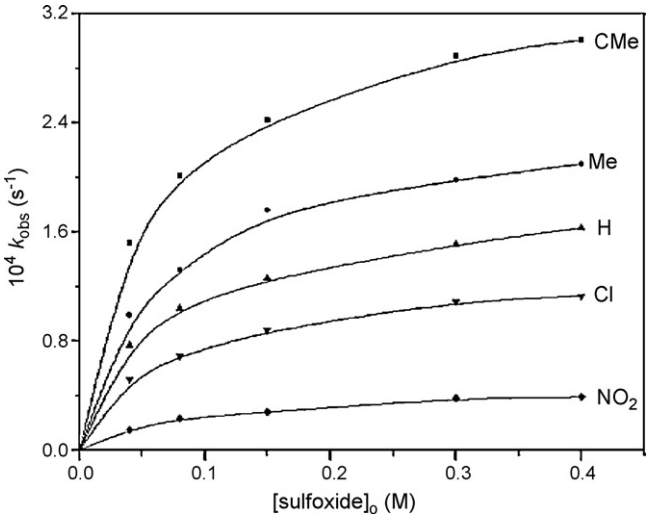

Fig. 1. Plots of k_{obs} versus [sulfoxide]$_o$ showing saturation kinetics for the oxidation of *p*-XC_6H_4SOMe with H_2O_2 catalysed by **1a**. The lines are labeled with the substituent *X*.

The reaction rate for the **1a**-catalysed oxidation of MPSO with H_2O_2 is almost unaffected (Table 3) by the presence of N-phenyl-1-anthranilic acid, a free-radical inhibitor. The retardation of reaction rate by this inhibitor in the metal–cyclam complex catalysed epoxidation [44] and by ionol in the (salen)Co^{II} catalysed epoxidation [45] with *t*-butyl hydroperoxide have been taken in favor of free-radical oxidising species. Consequently, it may be inferred that free radicals are not involved in the rate-controlling step of the present reaction. The rate of the reaction increases with increase in water content in the solvent mixture (Table 3). A plot of log k_{obs} versus $1/\varepsilon$ is linear ($r = 0.997$) indicating a charge-separated transition state in the rate-determining step.

Table 3
Effects of N-phenyl-1-anthranilic acid and solvent composition in the **1a**-catalysed oxidation of MPSO by H_2O_2 at 25 °C[a].

10^3[Inhibitor]$_o$ (M)	$10^4 k_{obs}$ (s^{-1})	% Water[b]	$10^4 k_{obs}$ (s^{-1})
0.0	1.26 ± 0.01	10	0.84 ± 0.01
2.0	1.20 ± 0.02	20	1.26 ± 0.01
4.0	1.18 ± 0.02	30	1.83 ± 0.01
6.0	1.19 ± 0.03	40	2.72 ± 0.07
8.0	1.17 ± 0.02	50	3.92 ± 0.05

[a] General conditions: [**1a**]$_o$ = 0.0004 M; [H_2O_2]$_o$ = 0.004 M; [MPSO]$_o$ = 0.15 M.
[b] Rest was acetonitrile.

$$[(salen)Mn^{III}OOH] + ArSOMe \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(salen)Mn^{III}(OOH)(ArSOMe)] \quad (4)$$
$$(C_1) \qquad\qquad (C_2)$$

$$(C_2) \xrightarrow[slow]{k_2} [(salen)Mn^{III}]^+ + ArSO_2Me + OH^- \quad (5)$$

$$H^+ + OH^- \longrightarrow H_2O \quad (6)$$

Scheme 1.

The reactive species in the present study is already shown to be [(salen)Mn^{III}OOH] (Section 3.1). Based on the observed experimental features, we propose that the oxidation of sulfoxides by the (salen)Mn^{III}/H_2O_2 catalytic system proceeds by a mechanism (Scheme 1), similar to that we proposed for the oxidation of alkyl aryl sulfides by the same system [29]. The mechanism involves the reversible formation of a ternary complex (C_2) in which both peroxide and the sulfoxide are bound to the complex. Then the monooxidation of sulfoxide occurs by a nucleophilic attack of the sulfoxide to the peroxide followed by H_2O release, within the manganese peroxide–sulfoxide complex. The fact that the (salen)Mn^{III}/H_2O_2 system oxidizes both alkyl aryl sulfides and aryl methyl sulfoxides by a similar mechanism is also evident from the excellent linearity of the plot of $\log k_2$ of aryl methyl sulfoxides versus $\log k_2$ of aryl methyl sulfides (Fig. 2, $r = 0.996$, slope = 1.11 ± 0.17).

The proposed mechanism (Scheme 1) leads to the rate expression:

$$\frac{1}{k_{obs}} = \frac{1}{k_2 K}\frac{1}{[ArSOMe]_o} + \frac{1}{k_2} \quad (7)$$

where K, equal to k_1/k_{-1}, is known as oxidant–substrate complex formation constant and gives a measure of the binding affinity of the substrate to the oxidant and k_2 is the complex decomposition rate constant. Eq. (7) suggests that a plot of $1/k_{obs}$ versus $1/[sulfoxide]_o$ should be a straight line with definite intercept on the ordinate. The excellent linearity observed in the Lineweaver–Burk plots (Fig. 3) supports the given mechanism. The values of k_2 and K obtained from the slopes and intercepts of these plots are collected in Table 4. To get more insights into the mechanism, substituent and steric effect studies were carried out with substituted aryl methyl sulfoxides and substituted (salen)Mn^{III} complexes.

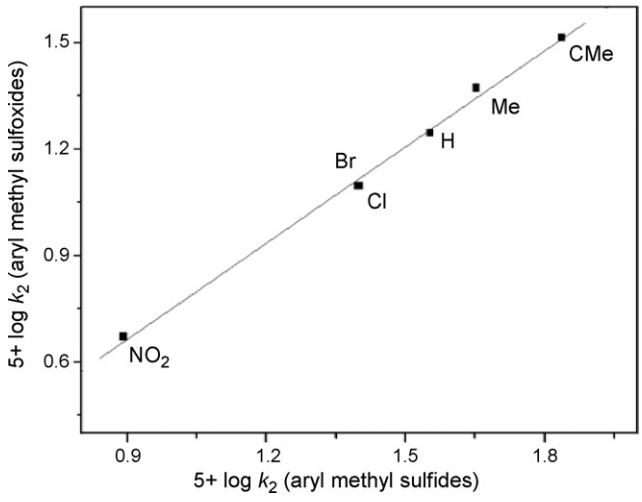

Fig. 2. Plot of $\log k_2$ of p-XC_6H_4SOMe versus $\log k_2$ of p-XC_6H_4SMe. The points are referred to by the substituent X.

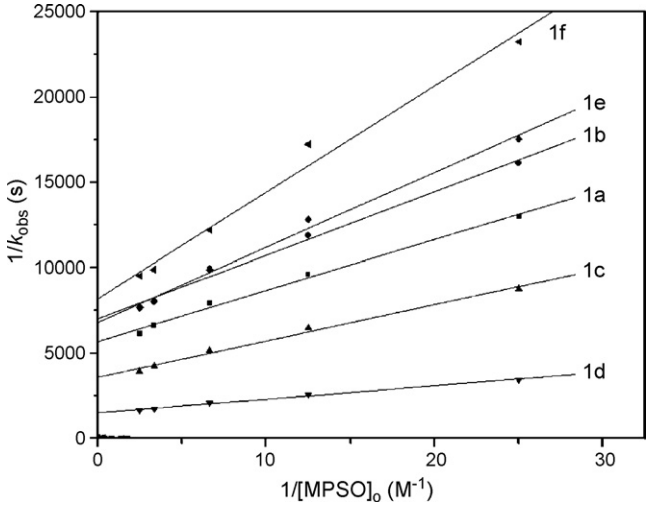

Fig. 3. Lineweaver–Burk plots for the oxidation of MPSO with H_2O_2 catalysed by **1a–f**.

3.3. Substituent- and steric-effect studies

The effect of substituents present at the 4-position of phenyl ring of aryl methyl sulfoxides on the reaction rate is implied from the k_2 values in Table 4. Electron-donating substituents accelerate the rate, while electron-withdrawing substituents retard it. Also, it is seen that though k_2 is highly sensitive to the nature of the substituents, K remains almost constant, thereby establishing that the decomposition of the ternary complex is the rate-determining step. The Hammett correlation of $\log k_2$ with σ_p values shows excellent linearity yielding a ρ value of -0.76 ± 0.03 (Fig. 4, $r = 0.997$). The negative ρ value indicates that the sulfur atom of the sulfoxide is more positively charged in the transition state than it is in the reactant, thus establishing the nucleophilic character of sulfoxide. This ρ value can be compared with (i) the ρ value (-0.85) observed for the oxidation of aryl methyl sulfides with the same catalytic system [29] and (ii) the ρ values (-2.44 and -2.57) observed for the

Table 4
Values of k_2 and K for the oxidation of p-XC_6H_4SOMe with H_2O_2 catalysed by **1a–f** at 25 °C in 80% acetonitrile–20% water.

Complex	X	$10^4 k_2$[a] (s^{-1})	K[a] (M^{-1})
1a	OMe	3.27	21.2
1a	Me	2.36	17.3
1a	H	1.76	19.1
1a	Cl	1.25	17.2
1a	Br	1.25	16.6
1a	NO_2	0.47	11.6
1b	H	1.43	18.8
1c	H	2.79	16.9
1d	H	6.63	19.0
1e	H	1.46	15.6
1f	H	1.21	13.3

[a] Calculated from the slope and intercept of Lineweaver–Burk plots.

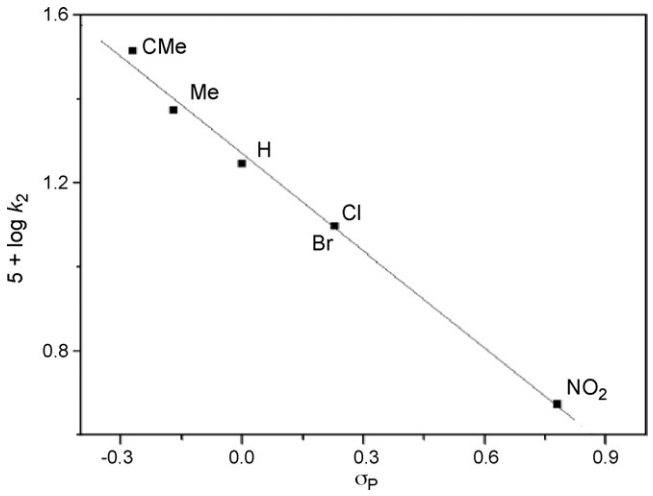

Fig. 4. Hammett plot for the **1a**-catalysed oxidation of *p*-XC_6H_4SOMe with H_2O_2. The points are referred to by the substituent *X*.

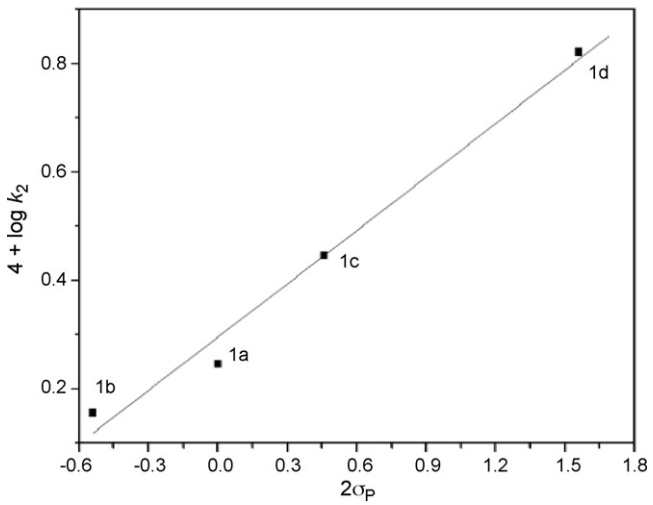

Fig. 5. Hammett plot for the oxidation of MPSO with H_2O_2 catalysed by **1a–d**.

oxidations of aryl methyl sulfoxides by oxo(salen)manganese(V) ion in (salen)Mn^{III}/PhIO [24] and (salen)Mn^{III}/NaOCl [28] catalytic systems. The first comparison reveals the less nucleophilic nature of sulfoxides than sulfides and the second comparison the less electrophilic character of (salen)Mn^{III}OOH species than oxo(salen)manganese(V) ion. It is worthwhile to mention here that all the three possibilities of ρ values for sulfoxide oxidations being same as [46,47], lower than [9,48,49] and higher than [24,28] those for sulfide oxidations are found in the literature and in all these studies, a common mechanism has been proposed for the oxidation of both the substrates.

The effect of changes in the electronic and steric nature of salen ligand on the rate of oxidation was also investigated using **1a–f** for the oxidation of MPSO. The k_2 values listed in Table 4 point out that electron-withdrawing substituents at the 5-positions of salen ligand enhance the rate, while electron-donating substituents retard the rate. The Hammett correlation of log k_2 with $2\rho_p$ shows a good correlation with a ρ value of 0.33 ± 0.03 (Fig. 5, $r = 0.992$). The positive ρ value indicates a build-up of negative charge on metal centre in the transition state of the rate-determining step. The k_{obs} and k_2 values measured at different initial concentrations of MPSO for the complexes **1a**, **1e** and **1f** (Tables 2 and 4) show that the presence of methyl or phenyl group at 7 and 7′ positions of salen ligand significantly reduces the rate of the reaction. Also, the lower values of *K* for **1e** and **1f** than **1a** imply that the association between the complex and sulfoxide is sensitive to steric environment of the complexes.

3.4. Reactivity selectivity principle

In order to test the applicability of RSP (reactivity selectivity principle—inverse relationship between the reactivity of a reagent and its selectivity among a set of similar substrates) in the present study, the k_2 values (Table 5) obtained from the Lineweaver–Burk plots for the reactions of various para-substituted phenyl methyl sulfoxides with H_2O_2 catalysed by each of the (salen)Mn^{III} complexes **1a–d** were subjected to Hammett correlations. The last row of Table 5 contains ρ values for substituent variation in the phenyl methyl sulfoxide for each complex, and the last column shows ρ values for substituent variation in the complex for each sulfoxide. The ρ values along the row are almost the same and so are the ρ values along the column, indicating that selectivity of sulfoxide or complex remains the same with increase in reactivity along the complex or sulfoxide series. This observation leads to the conclusion that RSP is not applicable in the present study. As a further verification, we subjected the k_2 values in Table 5 to a mathematical treatment formulated by Exner [50] using Eqs. (8) and (9):

$$\log k_{Fi} = a + b \log k_{Si} + \varepsilon_i \quad (8)$$

$$\Delta = \frac{\sum_i \log k_{Fi} - \sum_i \log k_{Si}}{N} \quad (9)$$

where k_{Fi} and k_{Si} are the rate constants for the reactions of fast and slow reagents (complexes) respectively with each sulfoxide, ε_i is the error of the log k_{Fi} versus log k_{Si} correlation, and Δ is the mean difference. The values of *b* and Δ were calculated for all of the six possible combinations of one fast and one slow reagent (among the

Table 5
Values of k_2 for the oxidation of *p*-XC_6H_4SOMe with H_2O_2 catalysed by **1a–d** at 25 °C in 80% acetonitrile–20% water[a].

X	Complex $10^4 k_2$[b] (s^{-1})				ρ[c] (*r*)
	1b	**1a**	**1c**	**1d**	
OMe	2.46	3.27	5.20	12.4	0.343 ± 0.021 (0.996)
Me	1.95	2.36	3.51	8.40	0.311 ± 0.030 (0.991)
H	1.43	1.76	2.79	6.63	0.326 ± 0.029 (0.992)
Cl	1.02	1.25	2.00	4.73	0.326 ± 0.029 (0.992)
Br	1.01	1.25	1.97	4.68	0.329 ± 0.026 (0.994)
NO_2	0.37	0.47	0.73	1.74	0.330 ± 0.024 (0.994)
ρ[d] (*r*)	−0.768 ± 0.015 (0.999)	−0.763 ± 0.030 (0.997)	−0.774 ± 0.041 (0.994)	−0.767 ± 0.042 (0.994)	

[a] General conditions: $[complex]_o = 0.0004$ M; $[H_2O_2]_o = 0.004$ M.
[b] Calculated from the intercept of Lineweaver–Burk plots.
[c] The values obtained by correlating log k_2 with $2\sigma_p$ for the complexes **1a–d** with a given sulfoxide.
[d] The values obtained by correlating log k_2 with σ_p for the various sulfoxides with a given complex.

Table 6
Results of correlations between $\log k_{Fi}$ and $\log k_{Si}$ according to Eq. (8).

Results	Complexes (F & S)					
	1a and **1b**	**1c** and **1b**	**1d** and **1b**	**1c** and **1a**	**1d** and **1a**	**1d** and **1c**
r	0.998	0.997	0.997	0.999	0.999	0.999
b	0.99 ± 0.04	1.00 ± 0.03	1.00 ± 0.04	1.01 ± 0.01	1.01 ± 0.01	1.00 ± 0.00
Δ	0.093	0.291	0.668	0.197	0.574	0.377

four complexes) with a series of similar substrates (six sulfoxides) (Fig. 6). The results summarized in Table 6 show an indifferent RSP (RSP(?)) in all the cases as the value of *b* is nearly one. As expected for a RSP(?), the lines in Fig. 6 are parallel to one another and produce no magic point. It may be mentioned here that a strong RSP has been observed in our earlier studies of oxidation of aryl methyl sulfides and sulfoxides with (salen)Mn^{III}/PhIO and (salen)Mn^{III}/NaOCl catalytic systems [22,24,26,28].

3.5. Comparison of reactivity of various catalytic systems towards organic sulfides and sulfoxides

Comparison of the studies of oxidations of aryl methyl sulfides and the corresponding sulfoxides by (salen)Mn^{III}/H_2O_2 [29,present study], (salen)Fe^{III}/PhIO [9,48], (salen)Mn^{III}/PhIO [21,24], (salen)Mn^{III}/NaOCl [26,28] and (salen)Cr^{III}/PhIO [25,49] catalytic systems discloses some interesting results. In all the five systems, both the substrates act as nucleophiles and the sulfides are more reactive. The same reactive species, (salen)Mn^{III}OOH in the first system and oxo(salen)M^{V} in the next three systems, oxidizes both sulfides and sulfoxides with a similar mechanism, Michaelis–Menten type in the first two systems and S_N2 type in the third and the fourth systems. In the fifth system, the mechanism is similar (S_N2 type), but the reactive species are different, oxo(salen)Cr^{V} for sulfide oxidation and oxo(salen)Cr^{V}–sulfoxide adduct for sulfoxide oxidation. The reaction constant (ρ) values observed for substituent variation in the para-position of phenyl ring of sulfides and sulfoxides show that sulfides are more sensitive in the first, second and fifth systems and sulfoxides are more sensitive in the third and fourth systems. The more sensitivity of sulfoxides in the third and fourth systems is in consistent with the Hammond postulate for a common S_N2 mechanism for both the substrates. That is, as the sulfides are electron-rich compared to the corresponding sulfoxides, they have an earlier transition state for interaction with the electrophilic oxo(salen)manganese(V) complex and will thus exhibit less positive charge on S atom and a weaker influence of the substituents, leading to a low ρ value. The less sensitivity of sulfoxides in the first and second systems can be attributed to the less nucleophilic character of sulfoxides compared to the corresponding sulfides in accordance with the observation in the earlier studies [51] that in the electrophilic oxidation by peroxides the reactivity of sulfoxides is considerably less affected by substituent effects than that of sulfides. The less sensitivity of sulfoxides in the fifth system is in contrast with the Hammond postulate for a common S_N2 mechanism and has been attributed to the poor electrophilic nature of oxo(salen)Cr^{V}–sulfoxide adduct compared to the oxo(salen)Cr^{V} complex.

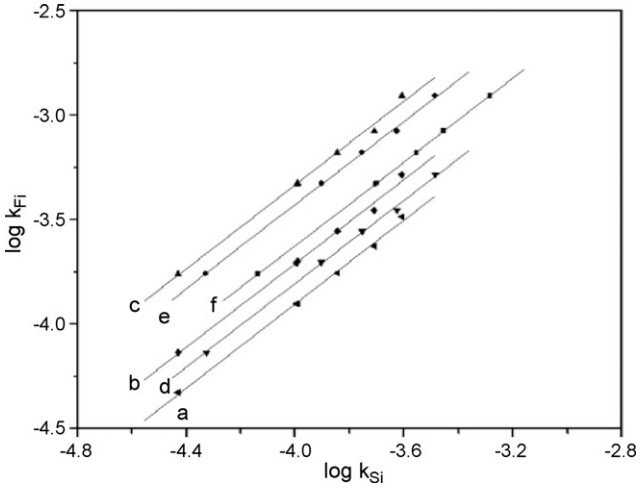

Fig. 6. Plot of $\log k_{Fi}$ versus $\log k_{Si}$ for the reactions of aryl methyl sulfoxides with H_2O_2 catalysed by (a) **1a** and **1b**, (b) **1c** and **1b**, (c) **1c** and **1a**, (d) **1d** and **1b**, (e) **1d** and **1a** and (f) **1d** and **1c**.

4. Conclusion

Aryl methyl sulfoxides are efficiently oxidized to the corresponding sulfones by the (salen)Mn^{III}/H_2O_2 catalytic system. Based on kinetic results and substituent effect studies with respect to both sulfoxide and complex a Michaelis–Menten type mechanism involving (salen)Mn^{III}OOH complex as reactive species has been proposed. The results in the present study have been compared with those obtained in our earlier studies of oxidation of organic sulfides and sulfoxides with the (salen)Mn^{III}/PhIO, (salen)Mn^{III}/NaOCl, (salen)Fe^{III}/PhIO and (salen)Cr^{III}/PhIO catalytic systems. Both Hammett correlations and Exner's method of mathematical verification point out an indifferent RSP in the present study.

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