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Kinetics and mechanism of (salen)Mn^{III}–catalysed hydrogen peroxide oxidation of alkyl aryl sulphides

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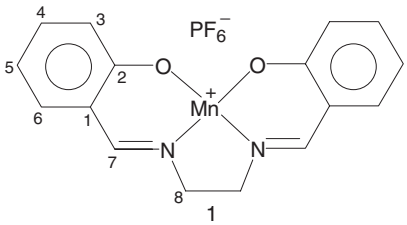
ABSTRACT: The kinetics of (salen)Mn^{III} complexes catalysed oxidation of aryl methyl and alkyl phenyl sulphides with hydrogen peroxide have been investigated at 25°C in 80% acetonitrile – 20% water spectrophotometrically. The reaction follows first-order kinetics in (salen)Mn^{III} complex and zero-order kinetics in hydrogen peroxide. The order of the reaction with respect to sulphide is fractional and saturation in reaction rate occurs at higher sulphide concentrations. The pseudo first-order rate constants have been analysed as per Michaelis–Menten kinetics to obtain the values of k_2, the oxidant-substrate complex decomposition rate constant, and K, the oxidant-substrate complex formation constant. The effects of nitrogenous bases, free radical inhibitor and changes in solvent composition have also been studied. A suitable mechanism, supported by electronic-oxidant and electronic-substrate effect studies, involving a manganese(III)-hydroperoxide complex as reactive species has been proposed. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: (salen)Mn^{III} complexes; hydrogen peroxide; organic sulphides; catalysed oxidation; mechanism

INTRODUCTION

Reactions of oxygen atom transfer from H_2O_2 and alkyl hydroperoxides are usually very slow[1] and such reactions are reported to be catalysed by an acid,[2] a solid support[3] and transition metal complexes.[4–8] In recent years, studies of metal complexes-catalysed oxygenations of alkanes, alkenes and sulphides by dioxygen and/or peroxides are being given considerable attention[9–17] in view of their relevance in understanding the mechanism of biological processes.[18] There are a number of reports on the peroxide oxidation of organic sulphides catalysed by metals and metal complexes.[12,14,19] Among the various peroxides employed in these studies, H_2O_2 is an attractive oxidant since it is less expensive, environmentally benign and gives only water as a by-product. We have recently investigated[20–28] the (salen)M^{III} complexes (salen = N,N'-ethylenebis(salicylideneaminato) and M = Mn, Cr, Fe or Ru) mediated oxygen atom transfer from PhIO and NaOCl to organic sulphur compounds. Compared to PhIO, H_2O_2 has been reported to afford higher yields of sulphoxides and minimal over oxidation to sulfone.[17] Moreover, with the same metal complex, PhIO and H_2O_2 are known[29] to produce different oxidising species. Although the Jacobsen-type (salen)Mn^{III} complexes have been used as catalysts for the H_2O_2 oxidation of sulphides, no detailed kinetic study has so far been attempted. Also, it will be interesting to know whether the (salen)Mn^{III} complexes-catalysed oxidation of sulphides by PhIO and H_2O_2 follows similar type of mechanism or not. Herein we report the results obtained from a detailed kinetic study on the oxidation of several alkyl aryl sulphides with hydrogen peroxide catalysed by (salen)Mn^{III} complexes (**1a**–**f**).



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a: Unsubstituted
b: 5,5'-$(OCH_3)_2$
c: 5,5'-Cl_2
d: 5,5'-$(NO_2)_2$
e: 7,7'-$(CH_3)_2$
f: 7,7'-$(C_6H_5)_2$

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EXPERIMENTAL

Materials

All the sulphides were prepared by known methods[20] and were purified by distillation under reduced pressure or recrystallisation from suitable solvents. Their purity was checked by comparing the boiling or melting points with the literature values. Further, the sulphides showed no impurity peaks in ^{1}H NMR spectra, and the HPLC analyses proved the presence of a single entity in each sulphide. (Salen)Mn^{III} complexes **1a–f** were prepared by the reported method.[10a,20] 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.

Kinetic measurements

The kinetic runs of the oxidation of aryl methyl and alkyl phenyl sulphides with hydrogen peroxide in the presence of **1a–f** were conducted in 80% acetonitrile-20% water at $25 \pm 0.1\,^{\circ}C$ under pseudo first-order conditions using 10- to 100-fold excess of sulphide over H_2O_2. Reaction mixtures for the kinetic runs were prepared by mixing the standard solutions of (salen)Mn^{III}, sulphide 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 Perkin–Elmer UV–Visible spectrophotometer (Lambda 3B) fitted with thermostated cell compartments.

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_∞) *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.[30] 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 $[sulphide]_o$.

Stoichiometry and product analysis

To a solution of **1a** (0.0004 M) and methyl phenyl sulphide (MPS) (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 sulphoxide in ~90% yield with negligible amount of sulfone, which established a 1:1 stoichiometry between MPS and H_2O_2 as represented by Eqn (1).

$$H_2O_2 + PhSMe \xrightarrow{(salen)Mn^{III}} PhSOMe + H_2O \qquad (1)$$

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), MPS (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 sulphoxide (~90%) with negligible amount of sulfone. 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 productanalyses carried out with other complexes and other sulphides also showed the formation of corresponding sulphoxide as the product. The percentage yields of sulphoxides determined from HPLC analyses ranged between 75 and 95 depending on the complex and the sulphide employed.

RESULTS AND DISCUSSION

Dismutation of hydrogen peroxide by (salen)Mn^{III} complexes

The (salen)Mn^{III} complexes **1a–f** show catalase-like activity with hydrogen peroxide. When an aqueous solution of H_2O_2 is added to a clear brown solution of **1a** (λ_{max} ~350 nm) at 25° C, the solution gets darkened associated with a brisk evolution of dioxygen as represented in Eqn (2).

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

Similar catalase-like activity has been reported for mono- and di-nuclear manganese,[13,31,32] iron[11,12] and cobalt[17b] complexes in acetonitrile. The oxygen evolution observed here stops after sometime and restarts on addition of a fresh quantity of H_2O_2, thereby establishing the catalyst-like nature of the complex. However, with subsequent additions of H_2O_2, the oxygen evolution becomes less and less vigour and after 10th or so addition the complex gets decomposed to unknown products as indicated by the bleaching of the complex solution. The dismutation of H_2O_2 is accelerated by the addition of nitrogenous bases such as 1-methylimidazole, 2-methylimidazole or pyridine as shown by the more vigorous evolution of oxygen. This observation is consistent with previous reports that nitrogenous bases stimulate catalase-like activities of iron and manganese complexes by binding to the metal centre.[33] On the other hand, addition of MPS greatly diminishes H_2O_2 dismutation and oxygen evolution.

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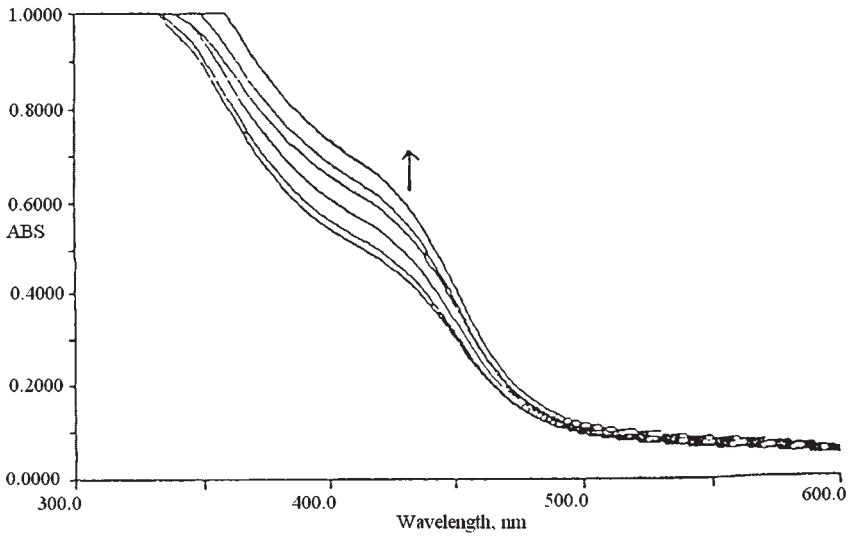

Figure 1. Spectral changes occurred during the mixing of H_2O_2 with an acetonitrile solution of **1a** at 5° C with time interval of 2 min

Under the present experimental conditions employed (i.e. lower complex concentration and [complex]/[H_2O_2] $\leq$1:30), the dismutation of hydrogen peroxide is insignificant as evidenced by the iodometric estimation of residual hydrogen peroxide.

Preliminary spectral studies

Addition of an aqueous solution of hydrogen peroxide (0.004 M) to a clear brown solution of **1a** (0.0004 M) at 25° C causes an instantaneous darkening in the brown colour of the solution. But, the darkening is not as much as intense as observed[20] when PhIO is stirred with the complex. The UV–Vis spectral analysis of the dark solution shows an absorption band with λ_{max} ~420 nm indicating the formation of an intermediate complex. The increase in concentration of this species with time is evident from the spectra recorded at 5°C (Fig. 1). When MPS (0.15 M) is added to this mixture, the spectral analysis shows the reverse changes (Fig. 2) that is, the species gets slowly decayed to finally give the original spectrum of **1a**. From these spectral observations it is clear that mixing of solutions of **1a** and H_2O_2 produces an intermediate species which is responsible for the oxidation of sulphide.

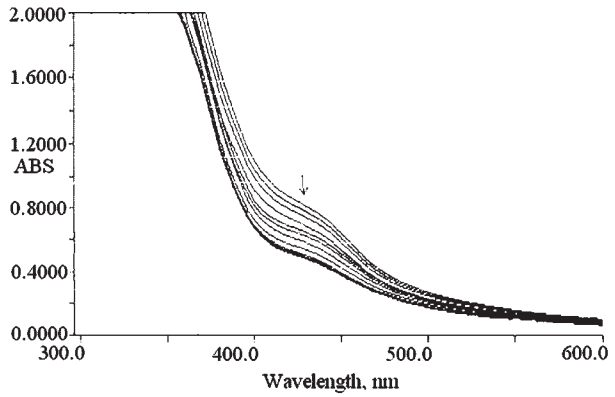

Figure 2. The absorption spectra showing the decay of the species formed from a mixture of **1a** and H_2O_2 in the presence of 0.15 M of MPS at 25° C in 80% acetonitrile-20% water

Kinetics of oxidation of aryl methyl sulphides

The kinetics of oxidation of aryl methyl sulphides with H_2O_2 in presence of **1a–f** was studied spectrophotometrically in 80% acetonitrile – 20% water at 25°C by monitoring the reaction at 400 nm. The pseudo first-order rate constants (k_{obs}) obtained for the oxidation of MPS are listed in Table 1. Comparison of rate constants for the uncatalysed and catalysed oxidation of MPS (first two entries) indicates that the presence of **1a** accelerates the reaction by a factor of ~45 times and hence the contribution of uncatalysed reaction between MPS and H_2O_2 can be neglected. Furthermore, if sulphide is added sometime after mixing H_2O_2 and complex, the rate constants are lower than those obtained when sulphide is added immediately by only 5–10% depending on the length of the interval period. Therefore, the decay of the complex in the absence of sulphide seems not to be substantial.

Inspection of rate data in Table 1 reveals that the rates are almost independent of initial complex concentration. This, coupled with the excellent linearity ($r > 0.995$) observed in ln (A_t–A_∞) *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 show that the reaction rate is independent of $[H_2O_2]_o$. The interesting feature of the present system is the fractional-order dependence of the reaction on the

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

10^2[MPS] (M)	10^3[H_2O_2] (M)	10^4[**1**]$_o$ (M)	$10^4 k_{obs}$ (s^{-1})
		1a	
15.0	10.0	—	0.15 ± 0.02[b]
15.0	10.0	10.0	6.87 ± 0.76[b]
8.0	6.0	2.0	2.07 ± 0.04
8.0	6.0	3.0	2.12 ± 0.04
8.0	6.0	4.0	2.10 ± 0.12
8.0	6.0	5.0	2.14 ± 0.13
8.0	6.0	6.0	2.08 ± 0.15
8.0	2.0	2.0	1.91 ± 0.11
8.0	3.0	2.0	1.89 ± 0.08
8.0	4.0	2.0	2.01 ± 0.13
8.0	5.0	2.0	2.09 ± 0.14
4.0	4.0	4.0	1.48 ± 0.12
8.0	4.0	4.0	1.95 ± 0.16
15.0	4.0	4.0	2.48 ± 0.26
30.0	4.0	4.0	3.08 ± 0.27
40.0	4.0	4.0	3.29 ± 0.34
		1b	
4.0	4.0	4.0	1.23 ± 0.11
8.0	4.0	4.0	1.63 ± 0.17
15.0	4.0	4.0	1.99 ± 0.15
30.0	4.0	4.0	2.50 ± 0.20
40.0	4.0	4.0	2.63 ± 0.22
		1c	
4.0	4.0	4.0	2.31 ± 0.22
8.0	4.0	4.0	3.14 ± 0.28
15.0	4.0	4.0	3.89 ± 0.34
30.0	4.0	4.0	4.65 ± 0.45
40.0	4.0	4.0	5.03 ± 0.41
		1d	
4.0	4.0	4.0	5.84 ± 0.37
8.0	4.0	4.0	7.36 ± 0.64
15.0	4.0	4.0	9.55 ± 0.78
30.0	4.0	4.0	11.6 ± 1.0
40.0	4.0	4.0	12.2 ± 1.1
		1e	
4.0	4.0	4.0	1.14 ± 0.12
8.0	4.0	4.0	1.56 ± 0.13
15.0	4.0	4.0	2.01 ± 0.17
30.0	4.0	4.0	2.46 ± 0.18
40.0	4.0	4.0	2.60 ± 0.25
		1f	
4.0	4.0	4.0	0.85 ± 0.04
8.0	4.0	4.0	1.17 ± 0.09
15.0	4.0	4.0	1.64 ± 0.12
30.0	4.0	4.0	2.00 ± 0.15
40.0	4.0	4.0	2.09 ± 0.13

[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.

initial concentration of MPS. The rate constants obtained for the oxidation of MPS catalysed by **1a–f** do not increase linearly with increasing concentration of sulphide (Table 1). It may be seen from Table 2 that this is the case with other aryl methyl sulphides also. The fractional-order dependence on [sulphide]$_o$ is further evidenced from the fractional slopes (Table 2) shown by the double logarithmic plots between k_{obs} and [sulphide]$_o$. The double reciprocal plots of k_{obs} versus [sulphide]$_o$ (Lineweaver–Burk plots) are excellently linear (Fig. 3, $r > 0.991$) thereby indicating that the reaction follows Michaelis–Menten type kinetics involving an intermediate complex formation between the oxidant and the sulphide.

Addition of a small amount of 2-methylimidazole, as low as 0.0004 M, to a solution containing **1a** and H_2O_2 in a 1:10 ratio, induced the dismutation of H_2O_2. Other nitrogenous bases, such as 1-methylimidazole and pyridine also showed a similar effect. Spectral analysis of the solution showed similar changes as depicted in Fig. 1, but with a much faster rate. When the experiment was repeated in the presence of MPS (0.15 M), the increasing trend of the absorbance continued, implying that the oxidation of MPS did not occur. These results suggest that the nitrogenous bases bind to the manganese centre irreversibly. It has been reported[12,13,32] that bases such as imidazole stimulate catalase-like activity of iron and manganese complexes through binding to the metal centre. The fact that the oxidation of sulphide does not occur in the presence of 2-methylimidzole implies that the nitrogenous base has greater binding affinity for metal centre than MPS, thereby indicating that the coordination of sulphide to the metal centre is a required condition for oxidation to occur. The reaction rate for the **1a** catalysed oxidation of MPS 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[34] and by ionol in the (salen)Co^{II} catalysed epoxidation[29b] with TBHP have been taken in favour 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[35] ($r = 0.994$). The observed effect is similar to that reported in the oxidation of organic sulphides by H_2O_2 in the presence of a diiron complex.[12]

Mechanism

In previous reports of metal complexes catalysed oxidation studies with peroxides, metal-oxo,[10b] metal-peroxo[9,36] and in some cases metal-independent peroxo radicals[11,17,29a] have been discussed as reactive species. The non-involvement of metal-independent peroxo reactive species in the present reaction is strongly indicated by the absence of any effect of *N*-phenyl-1-anthranilic acid. Furthermore, manganese complexes, among a set of metal complexes containing the same ligand, behave peculiarly by not preferring the metal-independent reactive species in oxidation reactions catalysed by them.[34,37] The fact that the oxidising species in the present study is a metal-derived one is also

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Table 2. Pseudo first-order rate constants for the oxidation of *p*-XC_6H_4SMe with H_2O_2 catalysed by **1a** at 25° C in 80% acetonitrile-20% water[a]

	10^4k_{obs} (s^{-1})					
	[sulphide]$_o$ (M)					
X	0.04	0.08	0.15	0.30	0.40	Order in sulphide[b]
OMe	2.99 ± 0.28	3.91 ± 0.28	4.75 ± 0.42	6.00 ± 0.54	6.51 ± 0.61	0.34
Me	1.95 ± 0.17	2.62 ± 0.21	3.15 ± 0.30	3.95 ± 0.33	4.12 ± 0.35	0.33
H	1.48 ± 0.12	1.95 ± 0.16	2.48 ± 0.26	3.08 ± 0.27	3.29 ± 0.34	0.35
F	1.41 ± 0.14	1.79 ± 0.14	2.29 ± 0.18	2.80 ± 0.23	2.95 ± 0.31	0.33
Cl	1.03 ± 0.06	1.38 ± 0.11	1.75 ± 0.11	2.15 ± 0.19	2.25 ± 0.19	0.34
Br	1.01 ± 0.07	1.34 ± 0.09	1.73 ± 0.13	2.17 ± 0.18	2.26 ± 0.21	0.36
Ac	0.59 ± 0.06	0.77 ± 0.06	0.98 ± 0.08	1.19 ± 0.12	1.25 ± 0.11	0.33
NO_2	0.34 ± 0.02	0.45 ± 0.05	0.55 ± 0.03	0.68 ± 0.06	0.72 ± 0.06	0.33

[a] General conditions: [**1a**]$_o$ = 0.0004 M; [H_2O_2]$_o$ = 0.004 M.
[b] Slope values of double logarithmic plots of k_{obs} *versus* [sulphide]$_o$.

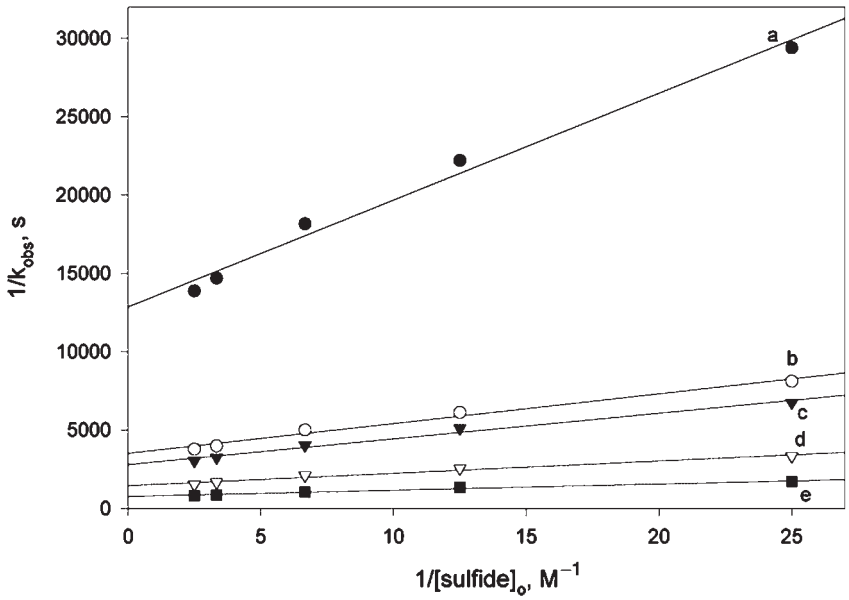

Figure 3. Lineweaver–Burk plots for the reactions involving (a) *p*-$NO_2C_6H_4SMe$ and **1a**, (b) MPS and **1b**, (c) MPS and **1a**, (d) *p*-$OMeC_6H_4SMe$ and **1a**, (e) MPS and **1d** with H_2O_2

established by the changes in the reaction rates with respect to changes in electronic and steric environment of the (salen)Mn^{III} complexes (*vide infra*).

The development of an absorption band with λ_{max} ~420 nm on mixing H_2O_2 with an acetonitrile solution of (salen)Mn^{III} complexes and the subsequent decay of this band on adding MPS (Figs 1 and 2) indicate that this new species may be the active species responsible for the oxidation of sulphides. The absence of a spectral band at λ_{max} ~530 nm, which has been reported to be formed in the (salen)Mn^{III}/PhIO and (salen)Mn^{III}/NaOCl systems,[20,25] clearly shows that the oxidising species here is not an oxo(salen)manganese(V) species. An oxidised dimeric intermediate, [(salpn)Mn^{IV}O]$_2$ has been proposed[38] as the reactive species for the [(salpn)Mn^{III}(acac)] catalysed epoxidation with H_2O_2. But this type of species, [(salen)Mn^{IV}O]$_2$ in the present system may be excluded because the salen ligand cannot adopt the *cis*-β-binding mode and also the steric demands of the salen ligand are too great.[38] One electron oxidised metal-peroxo complexes have also been shown as reactive

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

10^3[Inhibitor]$_o$ (M)	10^4k_{obs} (s^{-1})	% Water[b]	10^4k_{obs} (s^{-1})
0.0	2.48 ± 0.26	10	1.67 ± 0.09
2.0	2.40 ± 0.17	20	2.48 ± 0.26
4.0	2.38 ± 0.11	30	3.69 ± 0.28
8.0	2.32 ± 0.15	40	5.61 ± 0.36
		50	7.85 ± 0.55

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

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intermediates in some manganese[11,34,39] and cobalt[5,40] complexes catalysed oxidation reactions using oxygen and/or peroxide. The formation of such a one-electron oxidised metal-peroxo complex, $[(salen)Mn^{IV}OOH]^+$, in the present study would result in the generation of free radicals which would complicate the reaction. But from the observed neat kinetics and the absence of free radicals, it can be assumed that the Mn^{IV}-peroxo complex is not the reactive species in the present system. Also, the one-electron oxidised metal-peroxo species have been postulated mostly in reactions involving alkyl hydroperoxides[39,40] or oxygen,[34] while in reactions involving H_2O_2,[9,10c,41] HOO—coordinated complexes are shown as reactive species. On the basis of foregoing arguments, it may be said that the active species responsible for the oxidation of sulphides in the present study is presumably a Mn^{III}-hydroperoxide, $[(salen)Mn^{III}OOH]$, the formation of which can be shown as,

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

EPR analysis of the mixture of H_2O_2 and **1a** at 5° C gave no signal as expected for a low-spin Mn^{III}-OOH intermediate. It may be pointed out here that intermediacy of similar $Mn^{III}OOH$[42] and Mn^{III}-peracid[43] complexes as reactive species has been postulated in the $(TPP)Mn^{III}Cl$ catalysed epoxidation of olefins with H_2O_2 and peracid, respectively. Moreover, an EPR active mononuclear low-spin Fe^{III}-OOH complex has been characterized as reactive intermediate in the oxidation of alkyl phenyl sulphides by H_2O_2 catalysed by a diiron complex.[12]

The reactivity of Mn^{III}-OOH intermediate (C_1) seems to be dependent on the complex/H_2O_2 ratio, that is, when the ratio was maintained between 1:10 and 1:30 smooth kinetics was obtained; at ratios less than 1:10 there was no reaction, while at ratios higher than 1:30 dismutation of H_2O_2 occurred to evolve O_2. These observations are in consistent with those made by Sawyer and coworkers.[44,45] They have also proposed that when the reaction is carried out in an oxygen atmosphere or in the presence of excess ROOH ($R = Bu^t$ or H), the reactive intermediates, $[(salen)Mn^{III}(OOBu^t)(HOAc)]$ produce an oxygen adduct, $[(salen)Mn^{IV}(OOBu^t)(O_2)(HOAc)]$ which oxidises cyclohexane to cyclohexanone. Participation of O_2 derived either from the dismutation of H_2O_2 or from the oxygen atmosphere in the reaction process has been suggested in some other studies also.[11,46] Involvement of such oxygen adduct as reactive species in the present system can be ruled out on the facts that (a) under the present experimental combinations of complex and H_2O_2 (between 1:10 and 1:30) the catalase activity and hence the generation of O_2 in solution was negligible, (b) the reaction was not carried out under oxygen atmosphere and (c) sulphoxide formation was noted even when the reaction was conducted in an inert (nitrogen) atmosphere. The observation that the evolution of dioxygen is greatly diminished in the presence of sulphide suggests that the reactive species C_1 is responsible for the catalase activity also. In the presence of excess H_2O_2 and in the absence of sulphide, the access of a second molecule of H_2O_2 to the $(salen)Mn^{III}OOH$ species leads to catalase activity as represented in Eqn (4).

The intermediate, $[(salen)Mn^{V}(OH)(OOH)]^+$, is formed only in the presence of excess H_2O_2 and intermediacy of such species has been proposed in the reactions[45] of hydroperoxides with $(salen)Mn^{III}(OAc)$ and $(PA)_2Fe^{II}$ (PAH = picolinic acid) to explain the observed catalase activity. In the presence of sulphide, there arises a competition between H_2O_2 and sulphide for the active species (C_1) and hence the catalase activity is diminished. Similar explanation has been offered for the dismutation of H_2O_2 and other alkyl hydroperoxides by Fe(II)[14b,,47] and Mn(III)[11,31] complexes. Thus we can conclude that this metal-based oxidant (C_1) is responsible for sulphide oxidation at lower H_2O_2 concentrations.

Based on the observed experimental features, the following mechanism (Scheme 1) is proposed for

$$\underset{(C_1)}{[(salen)Mn^{III}OOH]} + HOOH \xrightarrow{H_3O^+} [(salen)Mn^{V}(OH)(OOH)]^+ + 2H_2O \quad (4)$$

$$[(salen)Mn^{V}(OH)(OOH)]^+ \rightarrow O_2 + [(salen)Mn^{III}]^+ + H_2O$$

$$\underset{(C_1)}{[(salen)Mn^{III}OOH]} + R_2S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{(C_2)}{[(salen)Mn^{III}(OOH)(R_2S)]} \quad (5)$$

$$(C_2) \xrightarrow[slow]{k_2} [(salen)Mn^{III}]^+ + R_2SO + OH^- \quad (6)$$

$$H^+ + OH^- \rightarrow H_2O \quad (7)$$

Scheme 1

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the oxidation of sulphides by hydrogen peroxide in the presence of (salen)Mn^{III} complexes.

The proposed mechanism involves the reversible formation of a ternary complex (C_2) in which both peroxide and the sulphide are bound to the complex. Then the monooxidation of sulphide occurs by a nucleophilic attack of the sulphide to the peroxide followed by H_2O release, within the manganese peroxide sulphide complex.

Based on kinetic observations and the mechanism proposed, the following rate expression can be derived.

$$-\frac{d[C_1]_o}{dt} = \frac{k_2K[C_1]_o[R_2S]_o}{1 + k_1[R_2S]_o} \quad (8)$$

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. Such Michaelis–Menten kinetics have been observed in the (TPP)Mn^{III}Cl and (TMP)Mn^{III}Cl complexes catalysed LiOCl epoxidation of olefins[48] and pyridinium chlorochromate,[49] bis(2,2'-bipyridyl)copper(II) permanganate[50] and diiron complex catalysed H_2O_2[12] oxidations of organic sulphides. As H_2O_2 is present always in excess over **1**, the conversion of **1** to C_1can be considered quantitative on the facts that (a) the absorption changes observed during the mixing of H_2O_2 and **1** was instantaneous and no further increase in absorbance with time was noted at 25° C, (b) the initial absorbance of C_1 remained constant at varying $[H_2O_2]_o$, and (c) k_{obs} is independent of H_2O_2 concentration (cf. Table 1).

Thus, Eqn (8) can be written as

$$-\frac{d[\mathbf{1}]_o}{dt} = \frac{k_2K[1]_o[R_2S]_o}{1 + K[R_2S]_o} \quad (9)$$

As $[R_2S]_o >> [\mathbf{1}]_o$

$$k_{obs} = \frac{k_2K[R_2S]_o}{1 + K[R_2S]_o} \quad (10)$$

$$\text{Hence, } \frac{1}{k_{obs}} = \frac{1}{k_2K}\frac{1}{[R_2S]_o} + \frac{1}{k_2} \quad (11)$$

Equation (11) suggests that a plot of $1/k_{obs}$*versus* $1/[R_2S]_o$ should be a straight line with definite intercept on the ordinate. The excellent linearity observed in the Lineweaver–Burk plots in the present study supports the given mechanism. Also the proposed mechanism (Scheme 1) gets further support from substituent and steric effect studies carried out with alkyl aryl sulphides and substituted (salen)Mn^{III} complexes.

Substitutent-effect studies

The pseudo first-order rate constants obtained for the oxidation of several *p*-substituted phenyl methyl sulphides with H_2O_2 in the presence of **1a** are included in Table 2. Electron-donating substituents accelerate the rate, while electron-withdrawing substituents retard it. Using these rate constant values, the values of K and k_2 have been estimated for each sulphide from Lineweaver–Burk plots. An analysis of K and k_2 values listed in Table 4 suggests 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 ($r = 0.994$) yielding a ρ value of -0.85 ± 0.09 (Fig. 4). The correlation of log k_2 with σ^+/σ^- (slope $= -0.51 \pm 0.08$, $r = 0.983$) is not better than the σ_p correlation. The negative ρ value indicates that the sulphur atom of the sulphide is more positively charged in the transition state than it is in the reactant. The lower ρ value -0.85 observed in this reaction may be due to the weaker electrophilic character of Mn^{III}-OOH than the oxo(salen)manganese(V) complex,[20] which gave a ρ

Table 4. Values of k_2 and K for the oxidation of *p*-XC_6H_4SMe with H_2O_2 catalysed by **1a–f** at 25° C in 80% acetonitrile-20% water

S.No.	Complex	X	10^4k_2,[a] (s^{-1})	K,[a] (M^{-1})
1	**1a**	OMe	6.86	18.6
2	**1a**	Me	4.49	18.7
3	**1a**	H	3.57	17.1
4	**1a**	F	3.17	19.1
5	**1a**	Cl	2.51	16.7
6	**1a**	Br	2.50	16.3
7	**1a**	Ac	1.36	18.4
8	**1a**	NO_2	0.78	18.9
9	**1b**	H	2.85	18.5
10	**1c**	H	5.49	17.8
11	**1d**	H	13.2	19.1
12	**1e**	H	2.92	15.7
13	**1f**	H	2.45	12.9

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

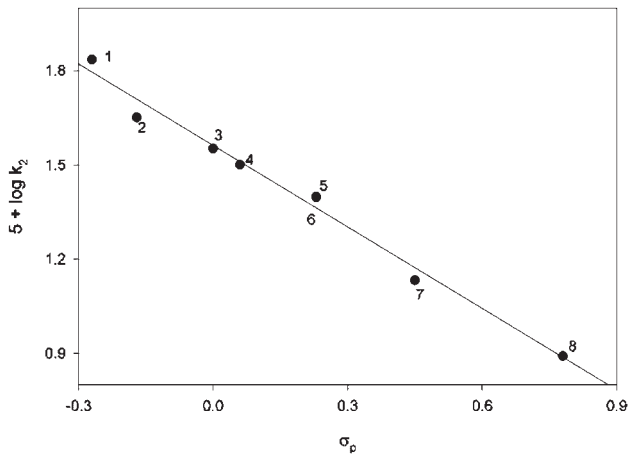

Figure 4. Hammett plot for the **1a** catalysed oxidation of aryl methyl sulphides with H_2O_2. The points are referred to by the same numbers as in Table 4

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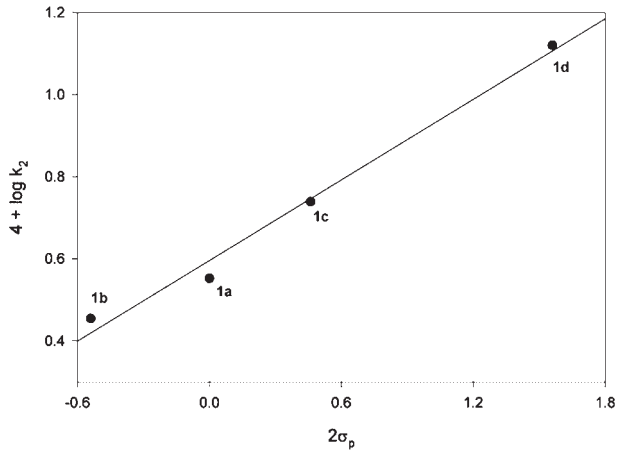

Figure 5. Hammett plot for the oxidation of MPS with H_2O_2 catalysed by **1a**–**d**

value of −1.85 in the oxidation of aryl methyl sulphides with (salen)Mn^{III}-PhIO system. Also, this ρ value is comparable to that of −0.55 obtained in the diiron complex catalysed oxidation of sulphides with H_2O_2, where intermediacy of a similar peroxide complex, Fe^{III}-OOH has been envisaged.[12]

The substituents present on 5 and 5'-positions of salen ligand greatly influence the electronic nature of (salen)Mn^{III} complexes and hence the rate of reactions they are catalysing.[20,51] Using the pseudo first-order rate constants obtained at different initial concentrations of MPS in presence of each of the complexes **1a**–**d**, K and k_2 values for each complex were estimated from Lineweaver–Burk plots and they are collected in Table 4. The Hammett correlation of log k_2 with $2\sigma_p$ shows an excellent linearity with a ρ value of 0.33 ± 0.11 (Fig. 5, $r = 0.994$). The positive ρ value indicates a build-up of negative charge on metal centre in the transition state of the rate-determining step. This ρ value is lower than that of 0.48 obtained in the (salen)Mn^{III}-PhIO system,[20] which indicates a lower charge transfer in the rate-determining step.

Steric effect studies

The oxidation of alkyl phenyl sulphides (C_6H_5SR'; R' = Me, Et, Pr^n, Pr^i and Bu^t) with H_2O_2 in presence of **1a** was studied by measuring k_{obs} at different initial concentrations of each sulphide. An analysis of the data given in Table 5 points out that the reactivity decreases in the order of increasing bulkiness of R'. The double logarithmic plots of k_{obs} versus [PhSR'] show that the order of the reaction increases from 0.35 for MPS to 0.63 for $PhSBu^t$. Here it may be pointed out that in the oxidation of sulphides with H_2O_2 catalysed by TiO(acac)$_2$,[52] a fractional order in MPS and a first-order in $PhSBu^t$ has been found and this observation has been attributed to the fact that the binding of sulphide with metal complex becomes difficult due to bulkiness of the *t*-butyl group. The steric effect exerted by these sulphides is also reflected in the magnitude of K values (Table 5), which decreases from MPS to $PhSBu^t$. Thus, it is clear that the binding affinity of these sulphides decreases with increase in the bulkiness of R'. Finally, the correlation of $\log(k/k_{Me})$ *versus* E_s, as per Taft's linear free energy-steric energy relationship[53] shows an excellent linearity ($r = 0.994$) yielding δ value of 0.34 ± 0.07. All these facts indicate that the reaction is sensitive to steric crowding at the reaction centre.

Substituents at the 7 and 8 positions of salen ligand in metal-salen complexes are reported to modulate significantly the steric environment of the complexes.[51] The k_{obs} values measured at different initial concentrations of MPS for the complexes **1a**, **1e** and **1f** show that the presence of methyl or phenyl group at 7 and 7' positions of salen ligand significantly reduces the rate of the reaction. The values of k_2 and K were also estimated and are included in Table 4. The lower values of K for **1e** and **1f** than **1a** implies that the association between the complex and sulphide is sensitive to steric environment of the complexes.

Table 5. Pseudo first-order rate constants for the oxidation of alkyl phenyl sulphides with H_2O_2 catalysed by **1a** at 25° C in 80% acetonitrile-20% water[a]

	$10^4 k_{obs}$ (s^{-1})				
[PhSR'] (M)	R' = Me	Et	Pr^n	Pr^i	Bu^t
0.04	1.48 ± 0.12	1.19 ± 0.09	0.73 ± 0.08	0.57 ± 0.05	0.14 ± 0.01
0.08	1.95 ± 0.16	1.62 ± 0.11	1.05 ± 0.07	0.78 ± 0.06	0.26 ± 0.02
0.15	2.48 ± 0.19	2.11 ± 0.16	1.50 ± 0.10	1.19 ± 0.09	0.41 ± 0.03
0.30	3.08 ± 0.27	2.62 ± 0.22	1.79 ± 0.13	1.53 ± 0.14	0.53 ± 0.05
0.40	3.29 ± 0.34	2.87 ± 0.27	2.07 ± 0.17	1.89 ± 0.18	0.62 ± 0.05
Order in sulphide[b]	0.35	0.38	0.44	0.52	0.63
$10^4 k_2$,[c] s^{-1}	3.57	3.16	2.40	2.10	1.04
K,[c] M^{-1}	17.1	14.6	10.7	8.85	3.89

[a] General conditions: $[\mathbf{1a}]_o = 0.0004$ M; $[H_2O_2]_o = 0.004$ M.
[b] Slope values of double logarithmic plots of k_{obs} *versus* $[\text{sulphide}]_o$.
[c] Calculated from the slope and intercept of Lineweaver–Burk plots.

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