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Kinetics and mechanism of (salen)Mn^{III}-catalysed oxidation of organic sulfides with sodium hypochlorite

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ABSTRACT: The oxidation of organic sulfides with several substituted oxo(salen)manganese(V) complexes was investigated in 90% acetonitrile–10% water and the reaction is second-order overall, first-order each in sulfide and complex. Electron-releasing substituents in sulfides and electron-withdrawing substituents in oxo(salen)manganese(V) complexes accelerate the rate of oxidation. The second-order rate constants for the oxidation of *p*-substituted phenyl methyl sulfides follow a linear Hammett relationship with $\rho = -1.85$. However, correlation between log k_2 and 2σ is excellent with $\rho = 0.48$ for the oxidation of thioanisole by substituted oxomanganese(V) complexes. The rate of oxidation of alkyl phenyl sulfides and dialkyl sulfides with oxo complexes was also examined and the reactions show a moderate steric effect. Substituent, acid and solvent effect studies reveal the operation of an S_N2 mechanism.

KEYWORDS: (salen)Mn^{III} complexes; sodium hypochlorite; organic sulfides; catalysed oxidation; mechanism

INTRODUCTION

Transition metal-catalysed transfer of oxygen atoms to organic substrates is of interest in the study of bioinorganic mechanisms and the development of efficient catalysts in the laboratory and industrial organic synthesis.[1] Currently, synthetic metallaporphyrins and metallasalens are receiving considerable interest as models of the cytochrome P-450 class of enzymes.[2] With single oxygen donors, e.g. dioxygen,[3] H_2O_2,[4] percarboxylic acids,[5] iodosylarenes,[6] hypochlorite,[7] sodium perchlorite[8] and activated *N*-oxides,[9] these compounds form high-valent oxometal complexes, which, like monooxygenases, are capable of oxygenating organic substrates. Several mechanisms have been proposed for oxygen transfer by hypervalent oxometal species. Oxygen transfer may proceed via electron transfer,[10] radical addition,[11] π-radical cation,[12] carbocation formation,[13] metallaoxetane formation[14] and combinations of these mechanisms.[15] Kochi and co-workers studied epoxidation of olefins with $Cr^{V}{=}O$ and $Mn^{V}{=}O$ complexes and showed that oxochromium(V)[16] has an electrophilic character and oxomanganese(V)[17] a radical-like character.

Although a large number of reports on the reactivity of oxometal complexes have appeared, most of them describe alkene epoxidation studies, and those dealing with the oxidation of compounds of heteroatoms are very limited.[18,19] The fact that cytochrome P-450 model complexes can readily catalyse the oxygenations of nitrogen and sulfur compounds makes the study of the reactivity of oxometal complexes towards organosulfur compounds[20] interesting and useful in understanding the mechanism of biologically important oxygen atom transfer processes. Recently, NaOCl, a cheap and readily available representative of the family of single-oxygen donors, has been used effectively in the presence of manganese–salen catalysts to epoxidize a variety of olefins.[21,22] Jacobsen and co-workers[21a,b] used chiral salen-based manganese(III) catalysts for epoxidation reactions with the terminal oxidants PhIO and NaOCl. They reported that both the terminal oxidants PhIO and NaOCl produce a common oxo intermediate, $[(salen)Mn^{V}{=}O]^{+}$. Adam and co-workers[22] studied the (salen)Mn^{III}-catalysed epoxidation of chiral allylic alcohols, oxidation of silyl enol ethers and ketene acetals with PhIO–NaOCl in the presence of 4-phenylpyridine *N*-oxide. They also established that in the absence of a chlorine source (CH_2Cl_2, Cl^-), the reaction between (salen)Mn^{III} complexes and PhIO–NaOCl leads to oxo(salen)manganese(V) complexes.[22c] Selective oxidation of sulfides to sulfoxides has been of continuing interest, for which numerous methods have been developed. Transition metal-catalysed sulfoxidations have been reported for oxidants such as H_2O_2, PhIO and *t*-BuOOH.[23] Oxidation of organic sulfides with aqueous sodium hypochlorite has been reported.[24] Only very few catalytic oxidation of organic sulfides with NaOCl have

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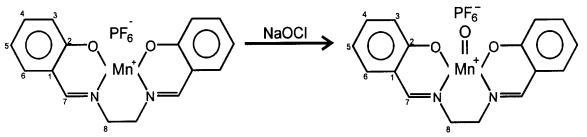
been described.[25] Siedlecka and Skarzewski[25b] studied the oxidation of sulfides with sodium hypochlorite catalysed by 2,2,6,6-tetramethylpiperidine-1-oxyl and reported that only 33% of sulfoxide was obtained without catalyst whereas 95% of sulfoxide was produced with catalyst.

We have initiated a systematic study on the oxygenation reactions of organosulfur compounds with oxometal complexes by taking Cr, Mn and Ru as metal ions. Recently we reported the mechanism of oxidation of organic sulfides and sulfoxides with PhIO catalysed by metal–salen complexes.[26–28] We initially proposed single electron transfer from organic sulfide to the oxometal ion as the rate-controlling step in the oxygen atom transfer reaction from several cationic oxo(salen)manganese(V)[26] complexes to sulfide. However, in a subsequent study, by comparing the reactivity of organic sulfides and sulfoxides towards the same oxidant, oxo(salen)manganese(V), a common mechanism involving the electrophilic attack of the oxygen of the oxidant at the sulfur centre of the substrate was proposed.[28] Similarly, the selective oxidation of organic sulfides to sulfoxides with oxo(salen)chromium(V) complexes proceeds through the electrophilic attack of oxygen at the sulfur center of the organic sulfide.[27]

In this paper, we report the kinetics and mechanism of the oxidation of thioanisoles with oxo(salen)manganese(V) complexes **2a–f** generated *in situ* from the corresponding $[(salen)Mn^{III}]^{+}PF_6^{-}$ complexes and NaOCl as represented in Eqn. (1).



(1)

1 2

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'-Ph_2

The active species in the present reaction is considered to be the oxo(salen)manganese(V) complex, as proposed by Jacobsen and co-workers[21a,b] and others[21c,22] in the $(salen)Mn^{III}$-catalysed NaOCl oxidation of achiral derivatives. We could not isolate this oxo(salen)manganese(V) complex and the present spectral data are similar to those in earlier reports.[17,26,28] Even though there is no report on the structural characterization of the oxo(salen)manganese(V) complex, recent theoretical work[29] suggested a triplet ground state for this species. Groves *et al.*[30a] and others[30b–e] have characterized oxomanganese(V)–porphyrin complexes in recent years. We chose the salen ligand because it is similar to porphyrin and the electronic and steric nature of the metal complex can be tuned by introducing electron-withdrawing and electron-releasing substituents and bulky groups in the ligand.

EXPERIMENTAL

Materials

Thioanisole, *para*-substituted thioanisoles and alkyl phenyl sulfides were prepared by known methods[26a,31] and were purified by distillation under reduced pressure or recrystallization from suitable solvents. The physical constants of these sulfides were found to be identical with literature values.[26a,31] Further, the sulfides showed no impurity peaks in ^1H NMR spectra, and the HPLC analyses proved the presence of single entity in each sulfide. The dialkyl sulfides purchased from Aldrich were used as such. Sodium hypochlorite (s.d.fine) was determined by an iodometric method. Acetonitrile (GR, 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 procedures.[17,28] The results of IR and UV–visible spectral studies of all the complexes were found to be identical with literature data.[17] The oxo(salen)manganese(V) complexes **2a–f** were obtained by mixing equimolar quantities of complex and sodium hypochlorite. As oxomanganese(V) complexes undergo autodecomposition, the solutions were prepared freshly for each kinetic run.

Kinetic measurements

The kinetic measurements were carried out in 90% acetonitrile–10% water at 20 ± 0.1 °C under pseudo-first-order conditions ([sulfide] >[oxo complex]) using a Perkin-Elmer UV–visible 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 sulfide in varying volumes so that in each run the total volume was 5 ml. The progress of the reaction was monitored by following the decay of oxo complex at 680 nm.

The rate constants were obtained from the slopes of linear 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 first-order self-decomposition rate constants $k_{1(dec)}$ of oxo(salen)manganese(V) complexes were determined from the first-order plots up to 50–60% of reaction. The plots for the decay of the oxo complex in the presence of sulfide were linear over 40% of reaction, and the pseudo-first-order rate constants $k_{1(obs)}$ were determined from the disappearance of the oxo complex up to this extent. The values of k_1 were obtained from $k_1 = k_{1(obs)} - k_{1(dec)}$ and the second-order rate constants were obtained from $k_2 = k_1/[sulfide]$. The

precision of the rate constant values in all the kinetic runs is given in terms of 95% confidence limit of Student's *t*-test. The thermodynamic parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were evaluated using the Eyring equation by the method of least squares.

Stoichiometry and product analysis

The stoichiometry of the reaction between the (salen)Mn^{V}=O complex and sulfide was studied under the experimental conditions ([**2a**] = 0.0026 M; [PhSMe] = 0.20 M). The reaction gave sulfoxide in ca 72% yield and Mn^{III} complex in ca 95% yield with a negligible amount of sulfone. Accordingly, the stoichiometry of the reaction can be represented by

$$O{=}Mn^{V}(salen)^{+} + PhSMe \longrightarrow Mn^{III}(salen)^{+} + PhSOMe \quad (2)$$

The reaction mixture from an actual kinetic run was subjected to vacuum evaporation and the residue was then extracted with chloroform. The extract was dried over anhydrous Na_2SO_4 and the solvent evaporated. The product was dissolved in methylene chloride and gas chromatographic analyses of the samples showed that sulfoxide was the sole product. The yield of sulfoxide, ranging from 70 to 85%, depended on the sulfide and oxomanganese(V) complex employed.

RESULTS AND DISCUSSION

The (salen)Mn^{III} complexes **1a–f** are all readily soluble in 90% acetonitrile–10% water. The electronic spectra of these clear brown solutions are characterized by absorption bands with $\lambda_{max} \approx 350$ nm tailing to beyond 400 nm. When a clear brown solution of (salen)Mn^{III} in acetonitrile–water is treated with equimolar quantities of sodium hypochlorite, it immediately turns dark brown, indicating the formation of oxomanganese(V) species.[21,22] The formation of oxo(salen)manganese(V) species is invariably associated with the following two changes: (i) the characteristic peak of (salen)Mn^{III} at $\lambda_{max} \approx 350$ nm disappears and (ii) a new absorption band at $\lambda_{max} \approx 530$ nm appears (Fig. 1). 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 thioanisole, the dark brown colour was discharged to original light brown within 15–20 min and phenyl methyl sulfoxide was isolated in 72% yield [Eqn. (3)].

$$PhSMe \xrightarrow[NaOCl]{(salen)Mn^{III}} PhSOMe \quad (3)$$

The absorption spectrum of the final solution coincided with that of the original (salen)Mn^{III} complex. We have tried to isolate the active (salen)Mn^{V}=O species in the following way. A solution of 2.6×10^{-3} M **1a** in acetonitrile–water was treated with an equimolar quantity of sodium hypochlorite at 20 °C. The dark brown solution of **2a** was poured directly into a pool of diethyl ether cooled to −40 °C. The dark brown solid was filtered at low temperature. The crude solid product was thermally labile and could not be purified by recrystallization. Upon dissolution, the crude solid was found to be impure compared to an *in situ* generated solution of **2a**, on the basis of their reported spectroscopic characterization. Therefore, the oxomanganese(V) complexes were generated *in situ* for the studies reported here.

Kinetics of oxygen atom transfer from oxomanganese(V) to sulfides

The kinetics of oxygen atom transfer from oxomanganese(V) complexes to sulfides was studied spectrophotometrically in 90% acetonitrile–10% water at 20 °C by monitoring the disappearance of oxo complex at 680 nm. Under pseudo-first-order conditions, excellent linear plots of $\log(A_t - A_\infty)$ versus time were obtained; from these plots, the pseudo-first-order rate constants $k_{1(obs)}$ and hence k_1 and k_2 were determined (Table 1). The excellent linearity of the $\log(A_t - A_\infty)$ versus time plots ($r > 0.995$) and at a constant initial concentration of sulfide, the constancy of k_1 values at different $[\mathbf{2a}]_0$ establish that the reaction is first-order in oxo(salen)-manganese(V) complex (Table 1). The pseudo-first-order

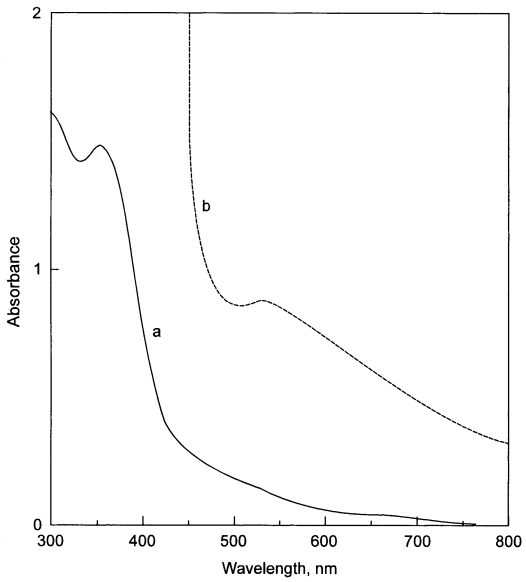


Figure 1. (a) Absorption spectrum of **1a** (0.0026 M) in 90% acetonitrile–10% water taken in a 1 cm cuvette; (b) absorption spectrum of oxo(salen)manganese(V) complex **2a** (0.0026 M)

Table 1. Rate constants for the oxidation of MPS by **2a** in 90% acetonitrile–10% water at 20 °C[a]

10^2[MPS]$_0$ (M)	10^3[**2a**]$_0$ (M)	$10^4k_{1(obs)}$ (s^{-1})[b]	$10^4k_{1(dec)}$ (s^{-1})[c]	10^4k_1 (s^{-1})[d]	10^3k_2 (M^{-1} s^{-1})[e]
10	1.00	10.0 ± 0.2	5.44 ± 0.09	4.56 ± 0.11	4.56 ± 0.11
10	1.60	9.97 ± 0.17	5.72 ± 0.16	4.25 ± 0.01	4.25 ± 0.01
10	2.00	9.58 ± 0.21	5.24 ± 0.09	4.34 ± 0.12	4.34 ± 0.12
10	2.60	9.96 ± 0.19	5.52 ± 0.03	4.44 ± 0.16	4.44 ± 0.16
10	3.00	10.2 ± 0.2	5.79 ± 0.16	4.41 ± 0.04	4.41 ± 0.04
10	3.60	10.3 ± 0.1	5.99 ± 0.05	4.31 ± 0.05	4.31 ± 0.05
5	2.60	7.75 ± 0.15	5.52 ± 0.03	2.23 ± 0.12	4.46 ± 0.24
15	2.60	11.8 ± 0.2	5.52 ± 0.03	6.28 ± 0.17	4.19 ± 0.11
20	2.60	14.1 ± 0.3	5.52 ± 0.03	8.58 ± 0.27	4.29 ± 0.14
40	2.60	22.0 ± 0.6	5.52 ± 0.03	16.5 ± 0.6	4.15 ± 0.15
50	2.60	26.8 ± 0.6	5.52 ± 0.03	21.3 ± 0.6	4.26 ± 0.12
100	2.60	51.3 ± 1.4	5.52 ± 0.03	45.8 ± 1.4	4.58 ± 0.14

[a] As determined by a spectrophotometric technique following the disappearance of oxomanganese(V) at 680 nm; the error quoted in k values is the 95% confidence limit of Student's t-test.
[b] Estimated from pseudo-first-order plots over 40% reaction.
[c] Estimated from first-order plots over 50–60% reaction in the absence of sulfide.
[d] Obtained as $k_1 = k_{1(obs)} - k_{1(dec)}$.
[e] Individual k_2 values estimated as k_1/[sulfide].

rate constant, k_1, for the oxidation of methyl phenyl sulfide (MPS) by the oxomanganese(V) complex increases with increase in substrate concentration. The plot of k_1 versus [MPS]$_0$ is a straight line passing through the origin (Fig. 2; $r = 0.997$). The double logarithmic plot of k_1 versus [MPS]$_0$ is linear ($r = 0.999$) with a slope of unity. Hence the reaction is overall second-order, first-order in each reactant. Similar results were obtained for the oxidation of substituted phenyl methyl sulfides with oxomanganese(V) complexes **2a–f**. Hence the rate law can be depicted as

$$\frac{-\mathrm{d}[\mathbf{2}]_0}{\mathrm{d}t} = k_2[\mathbf{2}]_0[\text{sulfide}]_0 \qquad (4)$$

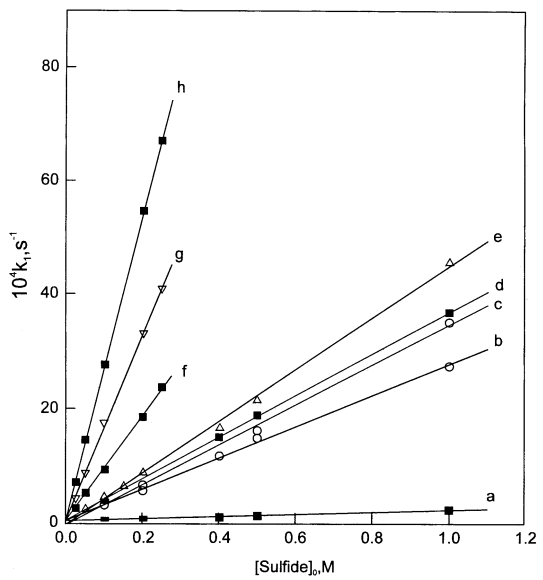


Figure 2. Plots of k_1 versus [sulfide] for the oxidation of (a) *p*-nitrothioanisole with **2a**; (b) thioanisole with **2b**; (c) diethyl sulfide with **2a**; (d) thioanisole with **2e**; (e) thioanisole with **2a**; (f) thioanisole with **2c**; (g) *p*-methoxythioanisole with **2a**; (h) thioanisole with **2d** in 90% acetonitrile–10% water at 20 °C; [**2**] = 0.0026 M

Addition of pyridine *N*-oxide (PyO), a donor ligand, to the dark brown solution of **2a** caused no change in the absorption spectrum of oxomanganese(V). The effect of donor ligand on the reaction rates was determined by measuring k_1 at various concentrations of added PyO. The rate data in Table 2 indicate that PyO has no appreciable effect on the reaction rate. The constant k_2 values at different [PyO] indicate that PyO does not bind with oxomanganese(V) species. If binding of PyO occurred as in the case of oxochromium(V) complexes,[16] then changes in the absorption spectra and reaction rates would have been observed. This conclusion is consistent with the observation of Powell *et al.*[9] that the manganese porphyrins lack affinity for a sixth axial ligand. Similar results were observed in the (salen)Mn^{III}-catalysed PhIO oxidation of olefins[17] and sulfides.[26]

To study the effect of acidity on the reaction rate, the rates at different concentrations of trichloroacetic acid were measured and are given in Table 3. The rate of oxidation increases significantly with increase in concentration of acid. To understand the nature of the transition state, the kinetics of oxidation of methyl phenyl sulfide were measured at various solvent compositions and the rate data are included in Table 3. The reaction rate increases as the amount of water in the solvent is increased.

Substituent effect

The second-order rate constants for the oxidation of *para*-substituted thioanisoles with **2a** are given in Table 4.

Table 2. Effect of pyridine *N*-oxide on the rate of oxidation of thioanisole by **2a** in 90% acetonitrile–10% water at 20 °C[a]

10^2[MPS]$_0$ (M)	10^3[**2a**]$_0$ (M)	10^2[PyO] (M)	$10^4k_{1(obs)}$ (s^{-1})[b]	$10^4k_{1(dec)}$ (s^{-1})[c]	10^4k_1 (s^{-1})[d]	10^3k_2 (M^{-1} s^{-1})[e]
10	2.60	2.5	9.74 ± 0.12	5.44 ± 0.07	4.30 ± 0.05	4.30 ± 0.05
10	2.60	5.0	10.0 ± 0.2	5.39 ± 0.05	4.61 ± 0.15	4.61 ± 0.15
10	2.60	10.0	9.70 ± 0.11	5.02 ± 0.10	4.68 ± 0.01	4.68 ± 0.01
10	2.60	20.0	10.7 ± 0.1	5.89 ± 0.08	4.81 ± 0.02	4.81 ± 0.02
10	2.60	25.0	10.3 ± 0.2	5.60 ± 0.11	4.70 ± 0.09	4.70 ± 0.09

[a] As determined by a spectrophotometric technique following the disappearance of oxomanganese(V) at 680 nm; the error quoted in k values is the 95% confidence limit of Student's t-test.
[b] Estimated from pseudo-first-order plots over 40% reaction.
[c] Estimated from first-order plots over 50–60% reaction in the absence of sulfide.
[d] Obtained as $k_1 = k_{1(obs)} - k_{1(dec)}$.
[e] Individual k_2 values estimated as k_1/[sulfide].

Table 3. Effect of adding acid and changing the solvent composition on the rate of oxidation of methyl phenyl sulfide by **2a** at 20 °C[a,b]

10^3[acid] (M)	10^4k_1 (s^{-1})[c]	CH_3CN:H_2O (%, v/v)	10^4k_1 (s^{-1})[d]
0.5	6.22 ± 0.03	90:10	8.58 ± 0.25
1.0	9.80 ± 0.27	85:15	15.8 ± 0.6
5.0	38.0 ± 1.3	80:20	18.9 ± 0.5
10.0	67.7 ± 2.3	75:25	23.0 ± 0.9
20.0	157 ± 6	70:30	28.2 ± 1.1

[a] General condition: [**2a**] = 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] [MPS] = 0.10 M; solvent = 90% CH_3CN–10% H_2O.
[d] [MPS] = 0.20 M.

Table 4. Second-order rate constants for the oxidation of *p*-XC_6H_4SMe and R_2S by **2a**–**d** in 90% acetonitrile–10% water at 20 °C[a]

No.	oxo(salen)Mn^V	X (E_{ox}, V)[b]	10^3k_2 (M^{-1} s^{-1})
1	**2a**	OCH_3 (1.26)	16.5 ± 0.7
2	**2a**	CH_3 (1.41)	10.2 ± 0.4
3	**2a**	H (1.53)	4.29 ± 0.14
4	**2a**	F (1.54)	3.61 ± 0.17
5	**2a**	Cl (1.55)	2.03 ± 0.06
6	**2a**	Br	1.66 ± 0.09
7	**2a**	COOH[c]	0.76 ± 0.08
8	**2a**	$COCH_3$ (1.73)	0.55 ± 0.08
9	**2a**	NO_2 (1.85)	0.18 ± 0.04
10	**2b**	H	2.91 ± 0.12
11	**2c**	H	9.20 ± 0.21
12	**2d**	H	26.8 ± 1.1
		R	
13	**2a**	Et	3.19 ± 0.11
14	**2a**	*n*-Pr	2.94 ± 0.14
15	**2a**	*i*-Pr	2.59 ± 0.14
16	**2a**	*n*-Bu	2.34 ± 0.10
17	**2a**	*t*-Bu	1.99 ± 0.08

[a] General conditions: [**2**] = 0.0026 M; [sulfide] = 0.20 M, unless noted otherwise.
[b] Oxidation potential values of sulfides taken from Ref. 33.
[c] [Sulfide] = 0.10 M.

Those sulfides containing electron-releasing groups in the benzene ring accelerate the rate whereas those with electron-withdrawing groups retard the rate. A plot of log k_2 versus σ_p shows an excellent correlation with the ρ value of -1.85 ± 0.04 (Fig. 3; $r = 0.998$). When σ^+/σ^- values are used a satisfactory correlation is obtained ($\rho = -1.05$, $r = 0.970$). Both σ^+ and σ^- values were employed simultaneously in the plot of log k_2 with σ^+/σ^-. Thus a better correlation is observed with σ values than σ^+/σ^- values. 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 atom in the transition state of the rate-determining step.[32] Further, the plot of log k_2 against the oxidation potential (E_{ox}) of sulfides[33] was linear with a correlation coefficient of $r = 0.980$ and a slope of -3.49.

The influence of the electronic effect of the oxidant on

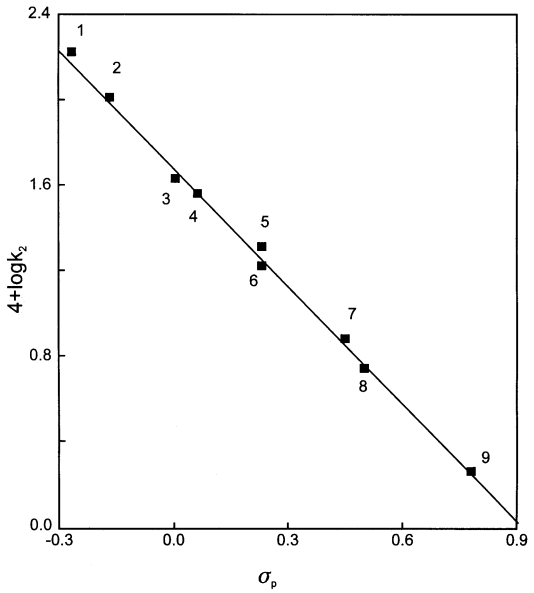


Figure 3. Hammett plot for the oxidation of aryl methyl sulfides by **2a**. The points are referred to by the numbers in Table 4

Table 5. Second-order rate constants for the oxidation of C_6H_5SR' by **2a–d** in 90% acetonitrile–10% water at 20 °C[a]

No.	R' (E_s)[b]	Oxo(salen)manganese(V) complexes 10^3k_2 (M^{-1} s^{-1})			
		2a	**2b**	**2c**	**2d**
1	Me (0.00)	4.29 ± 0.14	2.91 ± 0.12	9.20 ± 0.25	26.8 ± 1.1
2	Et (−0.07)	4.00 ± 0.24	2.50 ± 0.16	8.85 ± 0.23	25.1 ± 0.9
3	Pr^n (−0.36)	3.19 ± 0.16	1.96 ± 0.12	6.55 ± 0.22	22.3 ± 0.9
4	Pr^i (−0.47)	2.94 ± 0.15	1.63 ± 0.08	5.73 ± 0.12	18.0 ± 0.5
5	Bu^t (−1.54)	1.39 ± 0.11	0.63 ± 0.08	2.56 ± 0.12	9.55 ± 0.35
	δ[c]	0.31 ± 0.01	0.41 ± 0.02	0.36 ± 0.02	0.29 ± 0.03
	r	0.998	0.999	0.997	0.991

[a] General conditions: [**2**] = 0.0026 M; [sulfide] = 0.20 M.
[b] Taft's steric parameter taken from Ref. 34.
[c] Obtained by correlating $\log(k_2/k_{2Me})$ with E_s.

the rate of oxidation of thioanisole was studied with different 5,5′-substituted oxomanganese(V) complexes **2a–d**. The second-order rate constants are given in Table 4. Electron-releasing substituents at the 5-positions of the salen ligand decrease the rate and electron-withdrawing substituents enhance the rate of oxidation. The plot of log k_2 versus $2\sigma_p$ is linear with a slope of 0.48 ± 0.04 (Fig. 4; $r = 0.994$). The positive ρ value indicates the build-up of negative charge on the metal centre in the transition state of the rate-determining step.

Steric effect

The oxidation of alkyl phenyl sulfides C_6H_5SR' (R′ = Me, Et, Pr^n, Pr^i and Bu^t) with oxo(salen)manganese(V) complexes **2a–d** was studied with a view to understanding the effect of the bulkiness of alkyl group on the reaction rate. The rate constants listed in Table 5 show

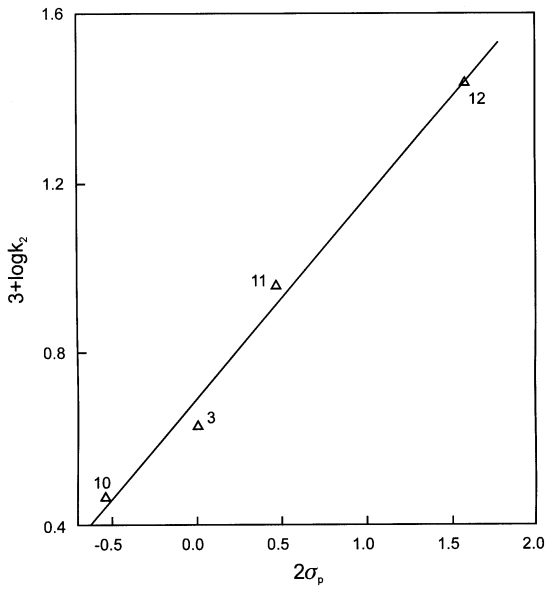


Figure 4. Hammett plot for the oxidation of thioanisole by substituted oxo(salen)manganese(V) complexes. The points are referred to by the numbers in Table 4

that the reactivity of alkyl phenyl sulfides decreases in the order PhSMe > PhSEt > $PhSPr^n$ > $PhSPr^i$ > $PhSBu^t$, indicating that the steric effect exerted by the increasing bulkiness of the alkyl group is predominant over the $+I$ (inductive) effect. Further, when $\log(k_2/k_{2Me})$ is plotted against Taft's steric substituent constant E_s,[34] an excellent correlation is obtained ($r > 0.990$). These facts indicate that the reaction is sensitive to steric crowding at the reaction centre, sulfur. Similar conclusions have been arrived at in the oxidation of alkyl phenyl sulfides by peroxoanions,[35] phenyliodoso diacetate,[36] Cr(VI),[31] bis(2,2′-bipyridyl)copper(II) permanganate[37] and (salen)Mn^{III}-catalysed PhIO.[26]

To understand the reactivity of alkyl sulfides towards **2a** and the role of steric effects in this reaction, the kinetics of oxidation of several dialkyl sulfides with **2a** were studied and the relevant data are included in Table 4. The observed kinetic data indicate that the dialkyl sulfides are oxidized more slowly than thioanisole and the reaction is sensitive to steric effects. Further, the effect of substituents at the 7-positions of the salen ligand of oxomanganese(V) complexes on the reaction rate was studied using **2a**, **2e** and **2f**. The rate data provided in Table 6 show that the presence of a methyl or phenyl

Table 6. Second-order rate constants for the oxidation of *p*-XC_6H_4SMe by **2a**, **2e** and **2f** in 90% acetonitrile–10% water at 20 °C[a]

X	Oxo(salen)manganese(V) complexes 10^3k_2 (M^{-1} s^{-1})		
	2a	**2e**	**2f**
OCH_3	16.5 ± 0.7	15.0 ± 0.4	14.7 ± 0.4
CH_3	10.2 ± 0.4	7.42 ± 0.27	7.00 ± 0.12
H	4.29 ± 0.14	3.87 ± 0.08	3.31 ± 0.07
F	3.61 ± 0.17	2.82 ± 0.08	2.56 ± 0.06
Cl	2.03 ± 0.06	1.47 ± 0.12	1.39 ± 0.05
Br	1.66 ± 0.09	1.35 ± 0.05	1.24 ± 0.04
COOH[b]	0.76 ± 0.08	0.64 ± 0.14	0.60 ± 0.01
$COCH_3$	0.55 ± 0.08	0.36 ± 0.03	0.32 ± 0.05
NO_2	0.18 ± 0.04	0.11 ± 0.02	0.09 ± 0.01

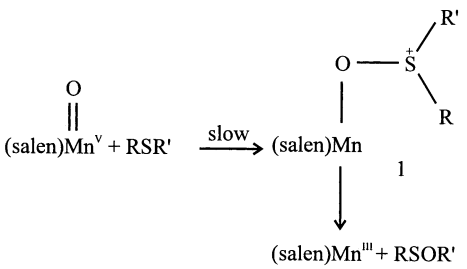
[a] General conditions: [**2**] = 0.0026 M; [sulfide] = 0.20 M, unless otherwise noted.
[b] [Sulfide] = 0.10 M.

group at the 7-positions slightly reduces the rate. Thus the steric effect observed in the present study is small. A similar observation has been reported in the oxidation of alkyl aryl sulfides with PhIO catalysed by (salen)Mn^{III} and (salen)Ru^{III} complexes.[26,38]

Mechanism

There are two possible mechanisms for the oxidation of organic sulfur compounds by metal ions and other oxidants. One is the nucleophilic attack of organic sulfide on the oxidant, known as the S_N2 mechanism. The second mechanism involves a single electron transfer (SET) from sulfide to oxidant. Oxidants such as peroxybenzoate,[39] hydroperoxidase,[40] Cr(VI),[31] Ce(IV)[41] and oxoruthenium(IV)[19] oxidize sulfides by a SET mechanism. The oxidation of sulfides by peroxoanions,[35] phenyliodoso diacetate,[36] bis(2,2′-bipyridyl)copper(II) permanganate,[37] molybdenum peroxypolyoxoanions,[42] sulfamyloxaridines,[43a] pyridinium hydrobromide perbromide,[43b] pyridinium halochromates,[44] permanganate[45,46] oxo(salen)manganese(V)[28] and oxo(salen)chromium(V)[27] follow an S_N2 mechanism. Further, the mechanism of oxidation may be a continuum between these two extremes, SET and S_N2.[47a] Pross established that the S_N2–SET continuum has general significance.[47b] However, for the oxidation of sulfides by PhIO catalysed by metallaporphyrin,[18] a clear distinction between the SET and S_N2 mechanisms has not been made, hence both mechanisms have been proposed for this oxidation reaction.

In the present investigation, since we identified oxomanganese(V) species as the crucial intermediate for the catalytic oxidation, let us now consider how the oxygen atom is actually transferred from the oxo species to the sulfide in the rate-limiting step. The observed first-order dependence with respect to sulfide and the absence of kinetic saturation (even at the high concentration of sulfide) indicate that prior coordination of sulfide to oxomanganese(V) is unimportant. Substituent effect studies can give an insight into the mechanism of the $[(salen)Mn^{V}{=}O]^{+}$ oxidation of organic sulfides. In the present study a ρ value of -1.85 was obtained. In the oxidation of sulfides by hydrogen peroxide[48] ($\rho = -1.13$), periodate ($\rho = -1.40$), permanganate[45a] ($\rho = -1.52$), peroxydisulfate[35a] ($\rho = -0.56$), lead tetracetate[50] ($\rho = -2.1$), pyridinium halochromates[44] ($\rho = -2.1$), Lewis acid-catalysed permanganate[46] ($\rho = -1.11$), perruthenate[51] ($\rho = -0.66$), (salen)Mn^{III}-catalysed PhIO[28] ($\rho = -1.86$), and oxo(salen)chromium(V) complexes[27] ($\rho = -2.7$), an S_N2 mechanism has been postulated. On the other hand, in the oxidation of thioanisoles by *tert*-butyl *p*-chloroperoxybenzoate[39] ($\rho = -1.68$), Cr(VI)[31] ($\rho = -2.07$), singlet oxygen[52] ($\rho = -1.63$), peroxymonosulfate[53] ($\rho = -1.0$), isoalloxazine hydroperoxide[40] ($\rho = -1.68$), carboxylato-bound chromium(V)[54] ($\rho = -1.19$), oxo(phosphine)ruthenium(IV) complexes[19] ($\rho = -1.56$), Ce(IV)[41] ($\rho = -3.3$) and Fe(III)–polypyridyl complexes[55] ($\rho = -3.2$), a SET mechanism has been proposed. Hence the low or high magnitude of the ρ value cannot be taken as evidence for the operation of a SET or S_N2 mechanism in a particular reaction. According to Miller *et al.*,[40] a decision on reaction mechanism simply based on the magnitude of the ρ value cannot be reliable. Reactions[54–57] that involve rate-limiting SET from sulfur to yield radical cation intermediates are known to give better Hammett correlations when σ^+ substituent constants are used. In the present study, as log k_2 is better correlated with σ rather than σ^+/σ^-, a single electron transfer is not likely the rate-limiting step of the reaction. If the transition state resembles a radical cation, as predicted by the Hammond postulate[58] for a SET mechanism, a better correlation should have been observed with σ^+ values. Hence the observed better correlation of log k_2 with σ than σ^+/σ^- may be taken as a clue for the operation of an S_N2 mechanism in the present reaction.[46] Furthermore, the substituted oxo(salen)manganese(V) complexes **2a**–**d** display an excellent Hammett correlation of log k_2 with $2\sigma_p$ in favour of electrophilic attack of oxidant on the sulfide sulfur.[16] The excellent correlation of the rates of alkyl phenyl sulfides with E_s values may favour nucleophilic attack of sulfide on the oxidant.[59] The observed significant increase in the rate of oxidation with increase in the concentration of trichloroacetic acid demonstrates the electrophilic nature of the oxidant. The addition of acid leads to the protonation of the oxidant[28] and the protonated species is more electrophilic, thereby favouring the reaction. The rate enhancement with increase in the polarity of the medium indicates the formation of a charge-separated transition state which is in favour of the S_N2 mechanism for the oxo(salen)manganese(V) oxidation of organic sulfides. Similar results have been observed in the oxidation of aryl methyl sulfides with a similar oxidant, oxo(salen)chromium(V) complexes,[27] and in the PhIO oxidation of aryl methyl sulfides and sulfoxides catalysed by (salen)Mn^{III} complexes.[28] Further, from the linear log k_2 versus E_{ox} plot we can obtain useful information on the mechanism of the reaction by comparing the results observed in the present study with the recent observations made by Goto *et al.*[60] on sulfoxidation catalysed by high-valent



Scheme 1.

Table 7. Second-order rate constants and activation parameters for the oxidation of *p*-XC_6H_4SMe by **2a** in 90% acetonitrile–10% water at four temperatures[a]

	10^3k_2 (M^{-1} s^{-1})					
X	293 K	298 K	303 K	313 K	$\Delta H^{\neq}$ (kJ mol^{-1})	$-\Delta S^{\neq}$ (J K^{-1} mol^{-1})
OMe	17.3 ± 0.6	22.9 ± 1.1	33.4 ± 1.1	65.0 ± 1.2	48.7	125
Me	10.1 ± 0.4	15.2 ± 0.7	19.9 ± 1.0	42.1 ± 0.7	51.1	108
H	4.45 ± 0.16	6.12 ± 0.22	8.66 ± 0.31	17.8 ± 0.9	50.7	117
F	3.65 ± 0.11	5.02 ± 0.22	6.46 ± 0.51	13.9 ± 0.3	48.3	127
Cl	2.03 ± 0.10	2.64 ± 0.26	4.06 ± 0.21	8.70 ± 0.50	54.2	112
Br	1.64 ± 0.09	2.47 ± 0.18	3.66 ± 0.31	6.70 ± 0.20	51.0	124
COOH	0.76 ± 0.08	1.06 ± 0.09	1.56 ± 0.31	3.20 ± 0.10	52.7	125
$COCH_3$	0.56 ± 0.00	0.73 ± 0.11	1.16 ± 0.21	2.20 ± 0.00	51.0	133
NO_2	0.18 ± 0.08	0.32 ± 0.04	0.46 ± 0.10	1.10 ± 0.10	65.2	93.6

[a] General conditions: [**2a**] = 0.0026 M; [sulfide] = 0.10 M.

intermediates of heme enzymes. Goto *et al.*[60] observed a slope of −10.5 when the reaction proceeds through an electron transfer mechanism and −2.2 in the case of the reaction proceeding via direct oxygen transfer. Hence the observed slope of −3.5 in the present study is in favour of a mechanism proceeding through direct oxygen transfer. Based on similar arguments Sivasubramanian *et al.*[61] proposed a direct oxygen transfer mechanism for the oxo(salen)iron oxygenation of organic sulfides.

Based on the arguments presented above, the S_N2 mechanism shown in Scheme 1 is proposed for the oxidation of organic sulfides with sodium hypochlorite catalysed by (salen)Mn^{III} complexes. The proposed mechanism involves the incipient formation of an intermediate **1** in the rate-limiting electrophilic attack of the oxidant on the sulfide sulfur. Then the intermediate **1** decomposes to give (salen)Mn^{III} and sulfoxide as the product. The proposed S_N2 mechanism is supported by the acceleration of rate by electron-attracting groups on the 5,5′-positions of salen(**2c** and **2d**) and by electron-donating groups in aryl methyl sulfides.

The oxo(salen)manganese(V) oxidation of *para*-substituted phenyl methyl sulfides was carried out at four different temperatures, and the thermodynamic parameters evaluated using the Eyring equation are collected along with k_2 values in Table 7. The $\Delta H^{\neq}$ (48–65 kJ mol^{-1}) and $\Delta S^{\neq}$ (−125 to −93 J K^{-1} mol^{-1}) values are in favour of two electron transfer rather than single electron transfer in the rate-limiting step of the reaction.[27,62,63] Although the correlation between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ is poor ($r = 0.812$), a plot of log k_2 at 20 °C versus log k_2 at 40 °C is linear ($r = 0.997$, slope = 0.92 ± 0.03, $s = 0.048$) indicating that all the sulfides are oxidized by a similar mechanism.

CONCLUSION

An S_N2 mechanism has been elucidated for the oxidation of aryl methyl sulfides with sodium hypochlorite catalysed by (salen)Mn^{III} complexes by varying the electronic nature of the substrate and oxidant. Rate studies with alkyl phenyl and dialkyl sulfides show the operation of a moderate steric effect.

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