Pergamon

Tetrahedron Vol. 51, No. 46, pp. 12677-12698, 1995
Elsevier Science Ltd
Printed in Great Britain
0040-4020/95 $9.50+0.00

0040-4020(95)00825-X

Mechanism of Oxidation of Organic Sulphides by Oxo(salen)manganese(V) Complexes

Arunachalam Chellamani,[a*] Nainamohamed Ismail Alhaji,[a] Seenivasan Rajagopal,[b*] Ranganathan Sevvel[c] and Chockalingam Srinivasan[c]

[a]Department of Chemistry, Manonmaniam Sundaranar University, Tirunelveli-627 002, India

[b]School of Chemistry, [c]Department of Materials Science, Madurai Kamaraj University, Madurai-625 021, India

Abstract: The kinetics of oxygen atom transfer from several cationic oxo(salen)manganese(V) [salen = N,N'-ethylenebis(salicylidineaminato)] complexes to organic sulphides have been studied spectrophotometrically in acetonitrile at 25°C. The reaction follows an overall second-order kinetics, first-order each in sulphide and oxomanganese(V) complex. Electronic-substrate and electronic-oxidant effect studies reveal that the single electron transfer from sulphide to the oxo complex is the rate-controlling step. The redox potentials of the couple Mn^{V}/Mn^{IV} have been estimated by applying Marcus theory to the experimentally observed rate constants.

Introduction

Design of catalysts for selective and efficient oxidation of organic substrates is a field of current interest.[1] In this regard metal complexes of porphyrin and Schiff base ligands as catalysts have widely been explored in the past decades.[2] For the oxygenation reactions of organic substrates the metal oxo species are generated from transition metal complexes using dioxygen[3] and a wide variety of oxygen transfer agents including iodosobenzene,[4-6] percarboxylic acids,[7] hydrogen peroxide,[8] sodium perchlorite,[9] and activated N-oxides.[10,11] The oxygenation reactions of a substrate S using metal oxo complexes, in general, can be represented by eq.(1).

$$L_nM{=}O + S \longrightarrow SO + L_nM \qquad (1)$$

Oxygen transfer by hypervalent oxometal species has been proposed to proceed by electron transfer,[12,13] radical addition,[14] carbocation formation,[15] metallaoxetane formation,[16] or a combination of these mechanisms.[17] Kochi and co-workers have studied epoxidation of olefins with $Cr^{V}=O$ and $Mn^{V}=O$ complexes and have shown that oxochromium(V)[18] has an electrophilic character and oxomanganese(V)[19] a radical-like character. Oxidation of alkynes with oxo(salen)chromium(V) complexes has been proposed to involve a metallaoxetene intermediate.[20] Metallaoxetane has also been shown to be an intermediate in the epoxidation of alkenes with Ru^{III}(EDTA) and Ru^{III}(PDTA) complexes.[21]

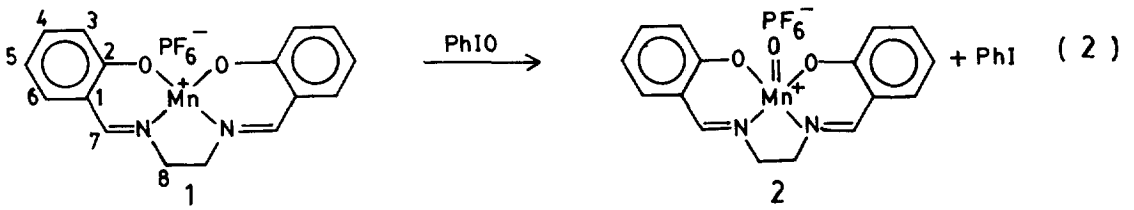
The preparation of a Mn substituted cytochrome $P\text{-}450_{cam}$ by Gelb *et al.*[22] and the suspected involvment of higher valent oxomanganese species in oxygen evolution in photosynthetic processes[23] have encouraged studies of oxygen atom transfer reactions catalysed by manganese complexes. Manganese(III) is also present in the active sites of enzymes[24] like super-oxide dismutase and azide-insensitive catalase which catalyse the redox reactions of oxygen species. Oxomanganese(V) complexes have been formulated as reactive intermediates in alkene epoxidation and hydroxylation reactions with porphyrin[9,14,25] and salen[19] ligand systems.

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 hetero atoms are very limited.[3,12,13] Many sulphur-containing compounds are present in natural biological systems and some play key roles in the activity of some enzymes.[26] These enzymes are often deactivated by active oxygen species. Further, the reactions of sulphur with oxygen are very complex because of the number of oxidation states of sulphur, which can lead to a wide variety of intermediates and products.[27] The fact that cytochrome P-450 can readily catalyse the oxygenations of nitrogen and sulphur compounds[28] makes the study of reactivity of oxometal complexes towards organosulphur compounds interesting and useful in understanding the mechanism of biologically important oxygen atom transfer process.

We have initiated a systematic study on the oxygenation reactions of organosulphur compounds with oxometal complexes by taking Cr,Mn and Ru as metal ions. In this report we have examined the kinetic and mechanistic aspects of the oxidation of organic sulphides by oxo(salen)manganese(V) complexes **2a-f** prepared in solution from a series of cationic (salen)Mn^{III} complexes **1a-f** as shown in eq.(2).

Experimental Section

Materials. Thioanisole and *p*-methoxy-, *p*-methyl-, *p*-chloro-, *p*-bromo- and *p*-nitrothioanisoles were prepared from the corresponding thiophenols (Aldrich/Fluka). All other *p*-substituted thioanisoles were obtained according to the literature procedure.[29-31] All the sulphides were purified by vacuum distillation/recrystallization from suitable solvents. The boiling point, melting point, n^{30} and d^{30} of these sulphides were found to be identical with literature values.[30,31]



1 2

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

Further, the sulphides showed no impurity peaks in ^1H NMR spectra, and the HPLC analyses proved the presence of a single entity in each sulphide. The dialkyl sulphides purchased from Aldrich were used as such.

The various salenH_2 analogues as Schiff base adducts were prepared from ethylenediamine and the corresponding salicylaldehyde (Aldrich) by standard methods[32] and were recrystallized from ethanol as bright yellow solids. o-Hydroxybenzophenone was prepared by Friedel-Crafts reaction of o-hydroxybenzoyl chloride with benzene.[33] o-Hydroxyacetophenone and pyridine N-oxide were commercial samples from Aldrich. Iodosobenzene was prepared by alkaline hydrolysis of iodobenzene diacetate according to the reported method.[34] Acetonitrile (GR, E.Merck) was first refluxed over P_2O_5 for 5 h and then distilled. Reagent grade methylene chloride (s.d. Fine) was purified by a standard method.[35]

Preparation of [(salen)Mn^{III}]$^+PF_6^-$ complexes, 1a-f. These complexes were prepared by a modified literature procedure.[19] The preparation of **1a** is given as a representative case. To a suspension of salenH_2 (4×10^{-3} M) in 40 mL of deaerated absolute ethanol was added a solution of KOH(8×10^{-3} M) dissolved in 10 mL of deaerated ethanol under nitrogen. To the resulting yellow solution was added dropwise a solution of $Mn(OAc)_2.4H_2O$ (4×10^{-3} M) in 10 mL of deaerated methanol. The formation of (salen)Mn^{II} complex was indicated by the change of colour of the suspension to dark yellow or orange. The suspension was stirred vigorously for 1 h at room temperature and refluxed for 3-4 h to ensure the completion of the reaction. The solution was then cooled and concentrated to 20 mL under reduced pressure. To this solution was added a solution of KPF_6 (4×10^{-3} M) in 20 mL of methanol and air was bubbled through the solution for 5-6 h. The resulting brown suspension was evaporated to dryness under reduced pressure. The Mn^{III} complex was obtained as a brown residue which was crystallized from a mixture of acetone and ethanol. The product was dried in vacuo for 2 h. Yield:63%. The other complexes **1b-f** were also prepared following similar procedures and obtained in 50-60% yields. The

IR- and UV-Vis spectral data of all the complexes were found to be identical with literature data.[19]

In Situ **Generation of [(salen)OMn]$^+PF_6^-$ Complexes 2a-f.** To a 5 mL acetonitrile solution containing $1.5x10^{-5}$ M of **1a** was added $1.5x10^{-4}$ M of finely powdered iodosobenzene and magnetically stirred for 5 min under nitrogen. The formation of oxomanganese(V) was shown by the darkening of brown colour (see Results). The oxomanganese(V) solution was filtered quickly at ice temperature to remove the undissolved iodosobenzene. As oxomanganese(V) complex undergoes autodecomposition the solutions were prepared freshly for each kinetic run.

Instrumentation. Electronic absorption spectra and kinetic data were measured with a Perkin-Elmer spectrophotometer (model Lambda 3B) retrofitted with Gilford accessories and interphased with Nexus 3AT6-SX computer. Thermostated temperature bath was used to maintain the temperature of the cell blocks at 25±0.1°C. Infrared spectra were recorded in a Perkin-Elmer spectrophotometer (model 783). Product analyses were done using a Netel gas chromatograph (model Omega Vir).

Product Distributions

In a typical experiment a 10-20 fold excess of the sulphide was weighed into a 25-mL round-bottom flask equipped with a magnetic stirrer. Acetonitrile (2 mL) was added, and the solution was deaerated with nitrogen for 5 min. A known volume (2-3 mL) of the oxomanganese(V) solution was then added. After stirring for 1 h, the solvent was removed. The residue was then extracted with ether. The ether extract was dried over anhydrous Na_2SO_4 and the solvent evaporated. The product was dissolved in methylene chloride and the gas chromatographic analyses of the samples showed that sulphoxide was the only product, the yield ranging between 60-70% depending on the sulphide and oxomanganese(V) complex employed.

Kinetic Measurements

The kinetic studies were carried out in acetonitrile at 25°C under pseudo first-order conditions using 20-100 fold excess of the substrate and the temperature was maintained within ±0.1°C. Reaction mixtures for kinetic runs were prepared by quickly mixing the solutions of oxomanganese(V) and sulphide in varying volumes so that in each run the total volume was 5 mL. The reaction mixture was shaken well and transferred to the 1 cm thermostated quartz cuvette. The progress of the reaction was monitored by following the disappearance of oxomanganese(V) complex at 680 nm.[19] The same decay rate was obtained when the reaction was monitored at 530 nm also.

The rate constants were obtained from the slopes of linear 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 plots for the auto-decomposition of oxomanganese(V) were linear over more than 3 half-lives

and the first-order rate constants $k_{1(dec)}$ were determined from the disappearance of oxo complex upto 50% of reaction. For those runs carried out in the presence of the sulphides, the pseudo first-order rate constants $k_{1(obs)}$ were determined from the decay of oxo complex within first 20% of the reaction. The k_1 values appearing in all tables were then obtained[3] as $k_1=k_{1(obs)}-k_{1(dec)}$. The second-order rate constants were evaluated from $k_2=k_1/[Sulphide]$. The precision of rate constant values is given in terms of 95% confidence limit of the student's t test.[36] It is estimated that, owing to the relatively fast kinetics and the technique adopted, the rate constant values are difficult to be reproduced to better than ±15%.

Results

I. Oxidative conversion of Manganese(III) to Oxomanganese(V) Species. The stirring of a clear brown solution of (salen)Mn^{III} complexes **1a-f** in acetonitrile with iodosobenzene consistently led to the formation of oxomanganese(V) species **2a-f** as shown in eq.(2). The formation of oxomanganese(V) species is invariably associated with the following two changes: (i) the light brown colour gets darkened; and (ii) the characteristic peak of (salen)Mn^{III} at λ_{max} ~ 350 nm disappears and a new absorption band with λ_{max} ~ 530 nm appears (Figure 1). The dark brown solution, on standing, faded to the original light brown within 2-3 h. When thioanisole was added to the dark brown solution, the fading occured in less than 15-20 min and phenyl methyl sulphoxide was isolated in 70% yield (eq. 3). The absorption spectrum of the final solution coincided with that of the original (salen)Mn^{III} complex.

$$PhSMe \xrightarrow[PhIO]{(salen)Mn^{III}} PhSOMe + PhI \qquad (3)$$

The new absorption band with λ_{max} ~ 530 nm has been assigned to μ-oxomanganese(IV) dimer,[19] the formation of which is explained in eq.(4).

$$O{=}Mn^{V}(salen)^{+} + Mn^{III}(salen)^{+} \rightleftharpoons (salen)Mn^{IV}OMn^{IV}(salen)^{2+} \qquad (4)$$

However, Mn^{V} and Mn^{IV} species are spectroscopically indistinguishable.[37] The disproportionation of the μ-oxomanganese(IV) dimer back to the active oxomanganese(V) in eq.(4) clearly indicates that the μ-oxomanganese(IV) dimer merely serves as an alternate source of oxomanganese(V). We actually obtained a solid product from the dark brown solution of **2a** by pouring the solution into a pool of ether cooled to -40°C. The dark brown solid was filtered at low temperature. Upon dissolution, these isolated solids were impure compared to *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.

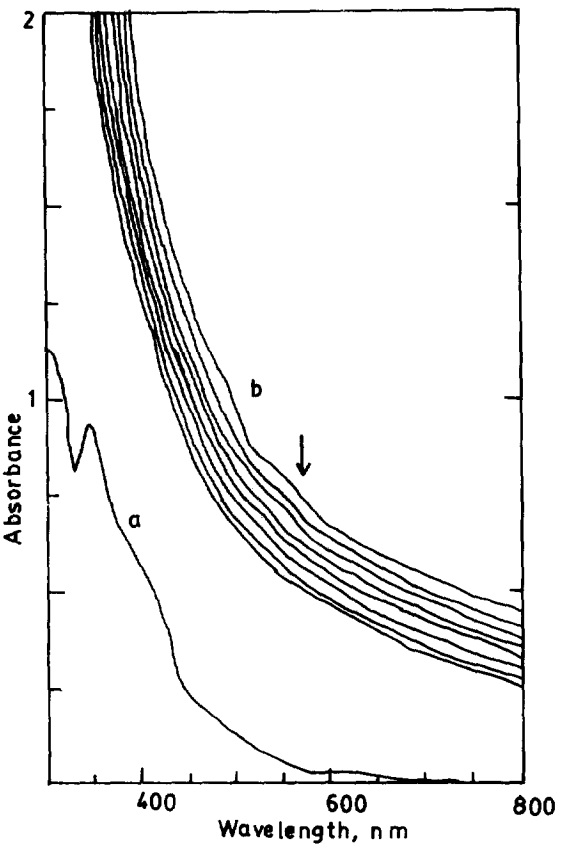


Fig.1. (a) Absorption spectrum of 0.0018 M **1a** in acetonitrile taken in a 1-cm cuvette. (b) Decay of oxo(salen)manganese(V) complex **2a** (0.0018 M) in the presence of thioanisole (0.04 M), taken at time intervals of 3 min.

II. Stoichiometric Oxidation of Sulphides with Oxomanganese(V). Sulphides are effectively oxidized by oxomanganese(V) cations. The course of the oxidation is easily revealed by the marked colour change of the acetonitrile solution from dark brown to light brown (see Figure 1). Spectral monitoring of the decay of oxomanganese(V) (0.0018 M of **2a**) indicated that the conversion of Mn^{V} to Mn^{III}, which normally took about 3 h for completion in the absence of sulphide, occured in less than 20 min in the presence of thioanisole (0.018 M). The resultant solution gave sulphoxide in ~70% yield and (salen)Mn^{III} complex in ~95% yield with negligible amount of sulphone. Accordingly, the stoichiometry for the oxidation of sulphides with oxomanganese(V) complexes can be represented by eq.(5).

$$O{=}Mn^{V}(salen)^{+} + PhSMe \longrightarrow Mn^{III}(salen)^{+} + PhSOMe \qquad (5)$$

III. Kinetics of Sulphide Oxidation with Oxomanganese(V). Reaction rates were measured in acetonitrile at 25°C spectrophotometrically by following the decay of oxomanganese(V) species at 680 nm. Using 20-30 fold excess of sulphide, excellent $\log(A_t-A_\infty)$ versus time,linear plots were obtained; from these, the pseudo first-order rate constants ($k_{1(obs)}$) and hence k_1 were determined.

At constant initial concentration of sulphide, nearly constant values of k_1 were obtained upon varying the initial concentration of **2a** (Table 1); this, coupled with the observation of linear $\log(A_t-A_\infty)$ versus time plots ($r > 0.995$) ensures that the order in **2a** is one. Inspection of data in Table 1 reveal that, for the oxidation of thioanisole at constant

Table 1. Rate constants for the oxidation of thioanisole by oxomanganese(V) complex **2a** in acetonitrile at 25°C[a].

[S] x 10^2, M	[2a] x 10^3, M	$k_{1(obs)}$[b] x 10^4, s^{-1}	$k_{1(dec)}$[c] x 10^4, s^{-1}	k_1[d] x 10^4, s^{-1}	k_2[e] x 10^3, $M^{-1}s^{-1}$
	0.83		5.27 ± 0.44		
	1.24		5.23 ± 0.24		
	1.65		4.72 ± 0.29		
	1.80		4.84 ± 0.32		
	2.02		5.16 ± 0.22		
	3.04		5.05 ± 0.19		
4.0	0.83	7.79 ± 0.38		2.52 ± 0.06	6.30 ± 0.15
4.0	1.24	7.69 ± 0.37		2.46 ± 0.13	6.15 ± 0.33
4.0	1.65	7.32 ± 0.58		2.60 ± 0.29	6.50 ± 0.73
4.0	1.80	7.47 ± 0.42		2.63 ± 0.10	6.58 ± 0.25
4.0	2.02	7.57 ± 0.11		2.41 ± 0.11	6.03 ± 0.28
4.0	3.04	7.73 ± 0.45		2.68 ± 0.26	6.70 ± 0.65
5.0	1.80	7.89 ± 0.62		3.05 ± 0.30	6.10 ± 0.60
10.0	1.80	11.2 ± 0.8		6.37 ± 0.48	6.37 ± 0.48
14.0	1.80	13.7 ± 0.9		9.12 ± 0.58	6.51 ± 0.41
20.0	1.80	18.2 ± 1.1		13.4 ± 0.78	6.69 ± 0.39
50.0	1.80	36.2 ± 3.8		31.4 ± 3.5	6.27 ± 0.70
100.0	1.80	67.7 ± 6.5		62.9 ± 6.2	6.29 ± 0.62

[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.[36] [b]Estimated from pseudo first-order plots over 20% reaction. [c]Estimated from first order plots over 50-60% reaction. [d]Obtained as $k_1=k_{1(obs)}-k_{1(dec)}$. [e]Individual k_2 values estimated as $k_1/[S]$.

2a concentration, k_1 values depend upon the initial concentration of thioanisole; indeed, a plot of k_1 versus [sulphide] yielded straight line passing through origin (Figure 2) indicating that the reaction is overall second-order, first-order in each reactant. Similar kinetics were observed for the oxidation of substituted

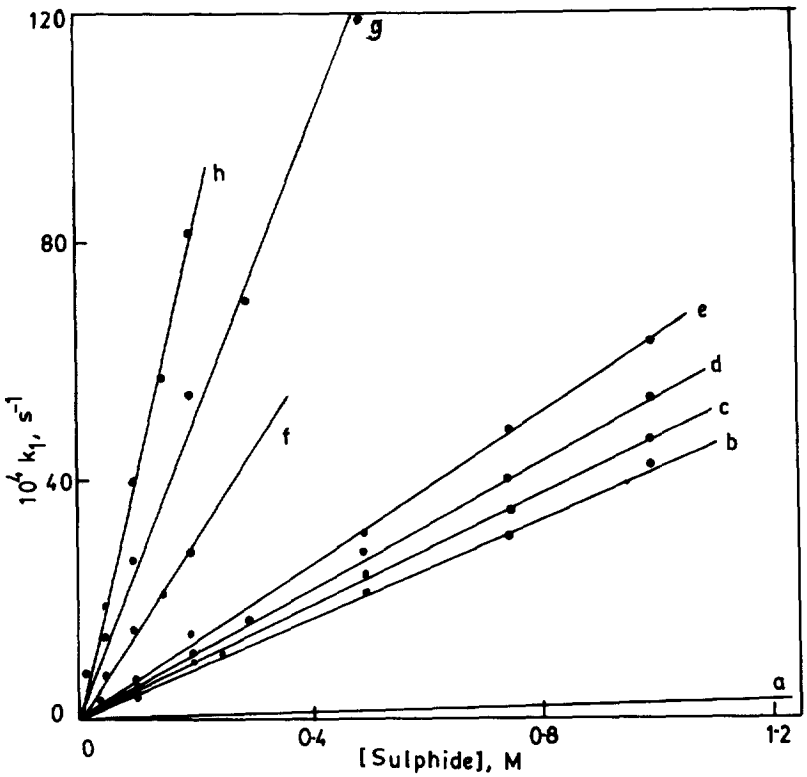


Fig.2. Plots of pseudo first-order rate constants, k_1, versus [sulphide] for the oxidation of (a) *p*-nitrothioanisole with **2a**, (b) thioanisole with **2b**, (c) diethylsulphide with **2a** (d) thioanisole with **2d**, (e) thioanisole with **2a**, (f) thioanisole with **2e**, (g) *p*-methoxythioanisole with **2a**, and (h) thioanisole with **2f** in CH_3CN at 25°C; [**2**]=0.0018 M.

thioanisoles with oxomanganese(V) complexes **2a-f** (Figure 2). The order dependence of other sulphides was checked by carrying out the reaction at different concentrations of para-substituted thioanisoles and dialkyl sulphides (Figure 2). Therefore, the rate law can be depicted as in eq.(6).

$$-d[2]/dt = k_2[2][\text{Sulphide}] \qquad (6)$$

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 for the oxidation of thioanisole with oxomanganese(V) species **2a** at various concentrations of added PyO. The

rate constant values listed in Table 2 indicte that PyO has no appreciable effect on the reaction rate. The constancy of k_2 values at different [PyO] points out that PyO is not binding with oxomanganese(V) species. If binding of PyO were occured as in the case of oxochromium(V) complexes,[18] then changes in absorption spectra and reaction rates would have been observed. This conclusion is in consistent with the observation of Bruice *et al.*[11] that the manganese porphyrins have lack of affinity for a sixth axial ligand. Similar results were observed in the oxomanganese(V) epoxidation of olefins.[19]

The effect of substituents at the para position of the phenyl ring of thioanisole was studied by taking several para-substituted thioanisoles. The second-order rate constants for the reaction of these para-substituted thioanisoles with **2a** are given in Table 3. Electron-releasing substituents in the phenyl ring accelerate the rate, while electron-attracting substituents produce the opposite effect. The log k_2 values show excellent correlation with σ_p (Figure 3;r=0.996;ρ=-1.86±0.19). The negative value of ρ indicates an accumulation of positive

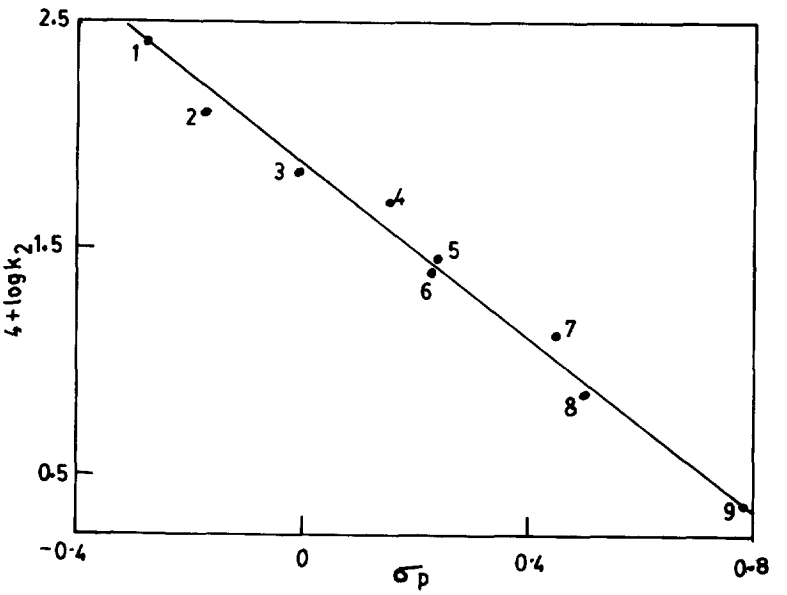


Fig.3. Hammett plot for the oxidation of substituted thianisoles by **2a**. The points are referred to by the same numbers as in Table 3.

charge at the sulphur centre, while the magnitude of ρ value indicates the extent of charge development on the sulphur atom in the transition state of the rate-determining step.[38] The correlations of log k_2 with first-ionization energies as well as with oxidation potentials of sulphides have also been attempted[39]. These plots were linear with

Table 2. Effect of pyridine N-oxide on the rate of oxidation of thioanisole by **2a** in acetonitrile at 25°C.[a]

[S] X 10^2, M	[2a] X 10^3, M	[PyO] X 10^2, M	$k_{1(obs)}$ X 10^4, s^{-1}	$k_{1(dec)}$ X 10^4, s^{-1}	k_1 X 10^4, s^{-1}	k_2 X 10^3, $M^{-1}s^{-1}$
	1.80	2.0		4.53 ± 0.48		
	1.80	5.0		4.41 ± 0.62		
	1.80	10.0		4.46 ± 0.51		
	1.80	15.0		4.34 ± 0.72		
	1.80	20.0		4.26 ± 0.27		
20	1.80	2.0	20.2 ± 1.5		15.7 ± 1.0	7.81 ± 0.52
20	1.80	5.0	20.2 ± 1.8		15.8 ± 1.2	7.89 ± 0.59
20	1.80	10.0	20.6 ± 1.8		16.1 ± 1.3	8.09 ± 0.68
20	1.80	15.0	20.4 ± 2.1		16.0 ± 1.4	8.01 ± 0.74
20	1.80	20.0	20.6 ± 0.8		16.0 ± 0.5	8.15 ± 0.33

[a]See the footnotes in Table 1.

Table 3. Second order rate constants for oxidation of XC_6H_4SMe and R_2S by oxo(salen)manganese(V) complexes **2** in acetonitrile at 25°C.[a]

No.	Oxo(salen)Mn^V (E^o, V)[b]	X (E^o, V)[c]	k_2 X 10^3, $M^{-1}s^{-1}$
1	**2a**	*p*-OCH_3 (1.26)	26.4 ± 1.6
2	**2a**	*p*-CH_3 (1.41)	12.0 ± 0.8
3	**2a** (0.751)(0.42)[d]	H (1.53)	6.69 ± 0.39
4	**2a**	*p*-F (1.54)	4.89 ± 0.12
5	**2a**	*p*-Cl (1.55)	2.68 ± 0.25
6	**2a**	*p*-Br	2.51 ± 0.16
7	**2a**	*p*-COOH[e]	1.29 ± 0.15
8	**2a**	*p*-$COCH_3$ (1.73)	0.72 ± 0.08
9	**2a**	*p*-NO_2 (1.85)	0.24 ± 0.09
10	**2b** (0.739)	H	4.37 ± 0.13
11	**2c** (0.744)	H	5.10 ± 0.58
12	**2d** (0.747)(0.280)[d]	H	5.67 ± 0.33
13	**2e** (0.770)(0.670)[d]	H	14.2 ± 0.1
14	**2f** (0.798)	H	40.8 ± 0.3
		R	
15	**2a**	Et	4.97 ± 0.18
16	**2a**	*i*-Pr	4.18 ± 0.11
17	**2a**	Bu	3.64 ± 0.27
18	**2a**	*t*-Bu	3.27 ± 0.23

[a]General conditions: [oxo(salen)Mn^V]=0.0018 M; [Substrate] = 0.2 M unless otherwise noted. [b]Reduction potential values of oxo(salen)Mn^V complexes estimated using Marcus equation (see text). [c]Oxidation potential values of sulphides taken from ref.39. [d]Reduction potential values of oxo(salen)Cr^V complexes taken from Ref.18. [e][substrate]=0.1 M.

correlation coefficients of 0.996 and 0.982 (Figure 4) with negative slopes.

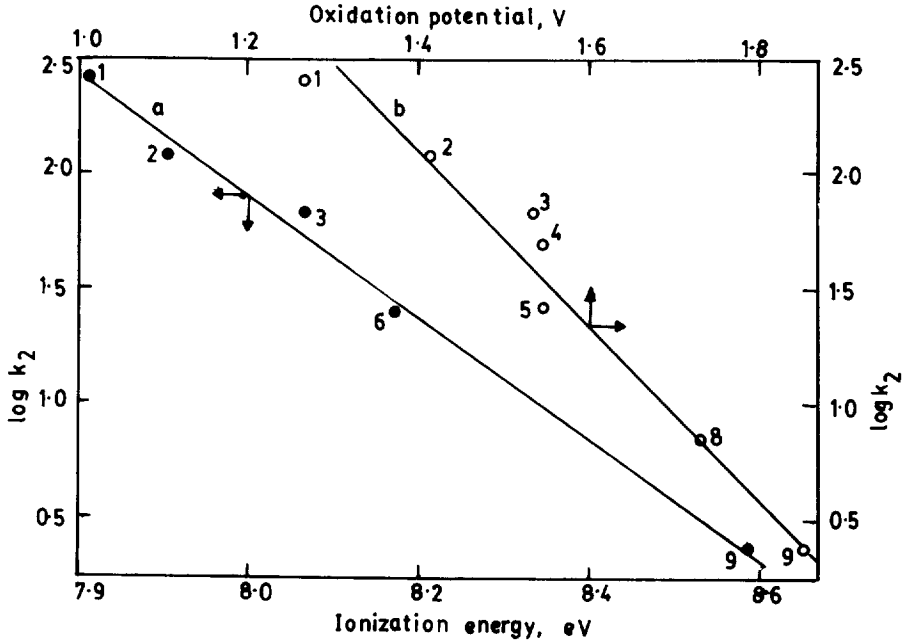


Fig.4. Plots of log k_2 versus (a) ionization energy (•) (values taken from ref. 39) and (b) oxidation potential (o) for the oxidation of substituted thioanisoles by **2a**. The points are referred to by the same numbers as in Table 3.

The electronic properties of oxomanganese(V) complexes can be modulated by having substituents at the 5-positions which are para to the pair of ligating oxygen atoms.[19] The effect of changes in the electronic nature of the oxidants was studied using oxomanganese(V) complexes **2a,b,e,** and **f** for the oxidation of thioanisole. The second-order rate constants for this study are also included in Table 3. It is seen that electron-withdrawing substituents at the 5-positions of salen ligand enhance the rate, while electron-releasing substituents retard it. Hammett correlation of log k_2 versus $\Sigma\sigma_p$ (where σ_p is the Hammett substituent constant for each of the para substituents on the salen ligand) shows a linear relationship with a slope of 0.47±0.08 (Figure 5; r=0.993). A plot of ln k_2 versus the reduction potential values E^o of Mn^V/Mn^{IV} couple calculated from the analysis of the kinetic data in terms of Marcus equation (vide infra) is also linear (Figure 6; r=0.999).

Discussion

Metal-salen complexes have been used as model systems to understand the mechanism of metal catalysed oxygen atom transfer reactions which

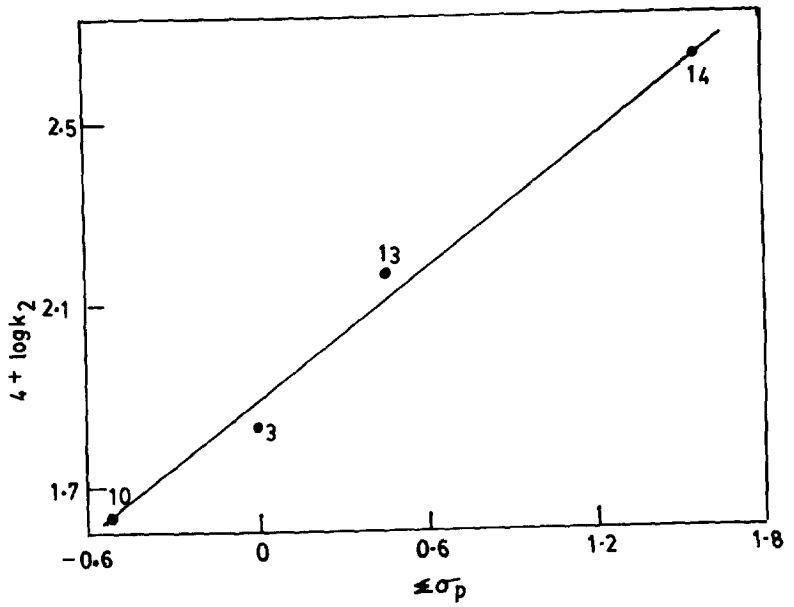


Fig.5. Hammett plot for the oxidation of thioanisole by substituted oxo(salen)manganese(V) complexes. The points are referred to by the same numbers as in Table 3.

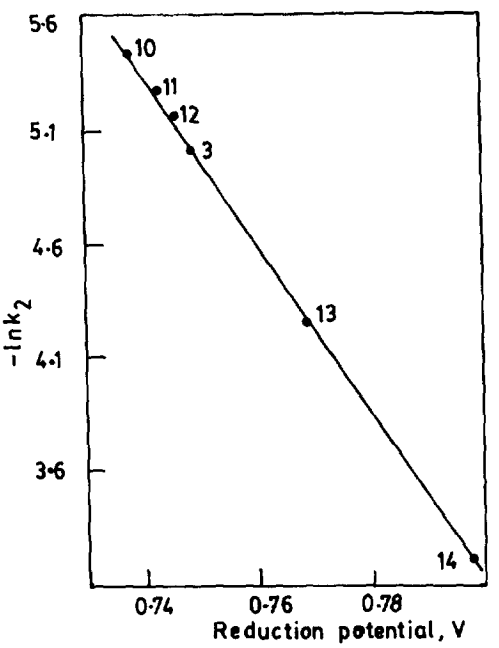
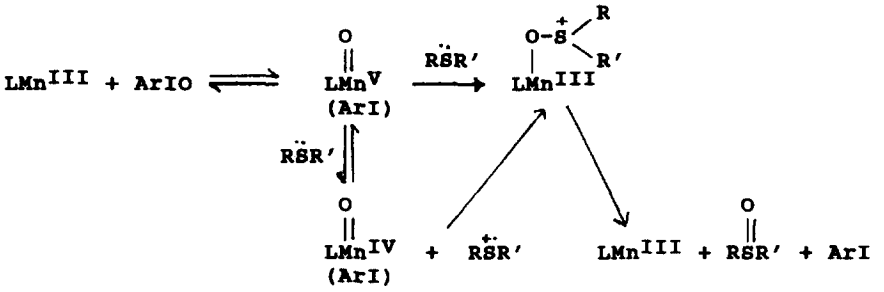


Fig.6. Plot of ln k_2 versus reduction potential of oxo(salen)manganese(V) complexes **2a-f**. The points are referred to by the same numbers as in Table 3.

play an important role in enzyme systems.[40] In the present study, organic sulphides are taken as a simple model system to comprehend the reactivity and mechanism of the oxometal complexes towards organic compounds containing hetero atoms.

Oxygen atom transfer to organosulphur compounds has been proposed to proceed by two different mechanisms. The oxidants such as peroxybenzoate,[41] hydroperoxidase,[42] Cr(VI),[43] Ce(IV)[44] and oxoruthenium(IV) complexes[13] oxidize sulphides by a single-electron-transfer (SET) mechanism. The oxidation of sulphides by peroxoanions,[45] molybdenum peroxypolyoxoanions,[46] sulfamyloxaridines,[47] phenyliodoso diacetate,[48] pyridinium chlorochromate[49] and permanganate[50] follow a S_N2 mechanism. However, for the oxidation of sulphides by PhIO catalysed by metalloporphyrins,[12] a clear-cut distinction between SET and S_N2 mechanisms has not been made and a common mechanism involving both the possibilities has been proposed (Scheme I).



Scheme I

We have investigated the reaction of oxomanganese(V) complexes **2** with sulphides in order to explore the nature of oxygen atom transfer. The principal processes underlying the colour and absorption spectral changes associated with eq. (3) can be summarized in Scheme II.

$$Mn^{III}L^{+} + PhIO \longrightarrow O{=}Mn^{V}L^{+} + PhI \qquad (7)$$

$$O{=}Mn^{V}L^{+} + PhSMe \longrightarrow PhSOMe + Mn^{III}L^{+} \qquad (8)$$

Scheme II

This type of oxygen rebound mechanism was originally proposed by Groves *et al.*[51] and has been subsequently established in the epoxidation of olefines[18,19] with chromium(III) and manganese(III) complexes. As the formation of oxomanganese(V) in eq.(7) has already been established (see Results), we can now consider how the oxygen atom is actually transferred from oxomanganese(V) to the sulphide in eq.(8).

I. Mechanism of the Oxygen Atom Transfer from Oxomanganese(V) to Sulphides. In the absence of other oxygen sources, as in the present

investigation, there is no doubt that the oxygen atom incorporated into the substrate is derived from the oxomanganese(V) ions. The k_1 values obtained for different initial concentrations of thioanisole (Table 1) and the linear plots in Figure 2 show that the kinetics saturation is not observed even at high concentration of sulphide employed. This suggests that in eq.(8) oxidation via preliminary coordination of sulphide to oxomanganese(V) can be ruled out. Further, the results obtained from the influence of electronic effects on substrate and oxidant revealed by substituent effect studies throw more light on the mechanism of oxygen atom transfer.

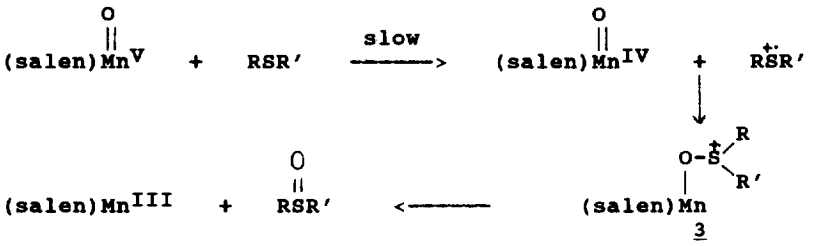
Substituent Effect Studies. The oxidation of para-substituted thioanisoles with **2a** was studied to evaluate the substrate electronic effects on thioanisole oxidation. The observed ρ value of -1.86±0.19 is analogous to the ρ values found for the oxidation of substituted thioanisoles by *tert*-butyl *p*-chloroperoxybenzoate[41] (ρ=-1.68), by Cr(VI)[43] (ρ=-2.07), by singlet oxygen[52] (ρ=-1.63) and by oxo(phosphine)ruthenium(IV) complexes[13] (ρ=-1.56). For all these cases, SET mechanism has been proposed. Correlations between log k_2 and ionization energies/oxidation potentials of sulphides have been taken as evidence for the SET mechanism in the oxidation of aryl methyl sulphides by Cr(VI)[43] and enzyme oxygenation of thioanosoles.[53] It has also been cautioned that the magnitude of the ρ value and good correlation of log k_2 with ionization energies/oxidation potentials of the substrates cannot be taken as conclusive evidence in favour of SET mechanism.[42] In the Ce(IV)[44] and Fe(III)-polypyridyl complexes[54] oxidation of organic sulphides ρ values of -3.3 and -3.2 respectively have been observed but SET mechanism has been postulated for these reactions. However, if we compare the ρ values observed for the oxidation of sulphides with similar oxidants, oxochromium(V) and oxomanganese(V), it may give a clue on the mechanism of the reaction. A ρ value of -3.2 is obtained in the oxochromium(V) oxidation[55] where electrophilic attack of chromium on sulphide in the rate-determining step has been postulated. Thus a low ρ value (-1.86) observed in the present case may point out single electron transfer in the rate-controlling step. The observed lower rate for dialkyl sulphides than that for thioanisloes (Table 3) is also in favour of SET mechanism. It is noteworthy to point out here that similar observation has been made in the oxidation of organic sulphides by Ce(IV).[44]

The effects of electron-donating and -withdrawing substituents at the 5-positions of salen ligand on the reaction rate shown in Table 3 can be interpreted as a reflection of a changing electron density in the oxomanganese(V) functionality. The electronic effect of oxomanganese(V) complexes on the oxidation of thioanisole was studied using **2a, b, e** and **f**. The positive ρ value of 0.47±0.08 obtained from the Hammett correlation of log k_2 versus $\Sigma\sigma_p$ (Figure 5) indicates the build-up of a negative charge on the metal centre in the transition state of the rate-determining step, as would be expected in the reduction of manganese(V)

to manganese(III).[38] It is pertinent to mention here that a ρ value of 0.49 has been reported for the oxidation of thioanisole with substituted oxo(phosphine)ruthenium(IV) complexes[13] where a SET mechanism has been proposed. The linear plot of ln k_2 versus the reduction potentials E^o of Mn^V=O complexes (Figure 6) also supports single electron transfer in the rate-determining step.

The effect of substituents at the 7-positions of salen ligand of oxomanganese(V) complexes on the reaction rate was studied using **2a,c** and **d** for the oxidation of thioanisole. The rate data in Table 3 show that the presence of methyl or phenyl group at 7-positions slightly reduces the rate. Thus the steric effect observed with Mn^V complexes is little which is contrary to the substantial steric effect noted in Cr^V complexes oxidation of alkynes.[20]

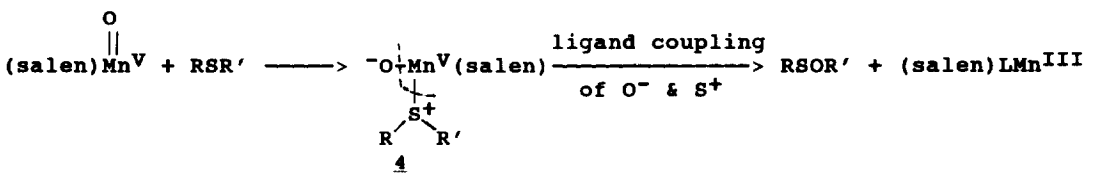
The following Scheme III is proposed for the oxidation of organic sulphides by oxo(salen)manganese(V) complexes to account for the kinetic data obtained. The mechanism envisages the formation of a cation radical in the slow step. The formation of cation radicals during



Scheme III

the oxidation of organic substrates has been firmly established in recent years.[44] Then the intermediate 3 decomposes to give Mn(III) and sulphoxide as the products. The rate acceleration by electron-withdrawing nitro substituents on the 5 and 5′ positions of salen (**2f**) and by the electron-donating *p*-methoxy group on thioanisole support this formulation.

Recently Lee and Chen[50] have proposed electrophilic attack of Mn on sulphide as the most probable mechanism for the MnO_4^- oxidation of organic sulphides. An alternate mechanism probable for the present kinetics of oxomanganese(V) oxidation of organic sulphides is shown in Scheme IV.



Scheme IV

The hypervalent intermediate 4 may be formed either in a single step due to electrophilic attack of Mn on electron rich sulphur or in two single electron transfer steps. Sulphoxide is formed due to ligand coupling of S^+ and O^- in the intermediate 4. Such a ligand coupling reaction has been postulated in the picolinic acid catalysed Cr(VI)[56] oxidation of organic sulphides and in other reactions[57] and reviewed recently by Oae and Uchida.[58]

II. Estimation of Redox Potential of Mn^{V}/Mn^{IV} Couple. In the present investigation, $O{=}Mn^{V}$ complex is produced at the time of reaction and is comparatively unstable. Hence the determination of the reduction potential of the Mn^{V} complexes is rather difficult. However, it can be estimated theoretically from the experimentally observed rate constants using Marcus theory of electron transfer.[59] The free energy change, ΔG, of the reaction is given in terms of the redox potentials of the reactants (eq.9).

$$\Delta G = E_{S^+/S} - E_{Mn^{V}/Mn^{IV}} \quad (9)$$

Thus if the value of ΔG is known, $E_{Mn^{V}/Mn^{IV}}$ can be obtained as the oxidation potentials of the sulphides are available and collected in Table 3. Marcus theory relates ΔG with the free energy of activation, $\Delta G^{\ddagger}$, through eq.(10),

$$\Delta G^{\ddagger} = \lambda/4\ (1+\Delta G/\lambda)^2 \quad (10)$$

where λ is the reorganization energy. The value of λ is the sum of two terms, the inner-sphere reorganization (λ_i) and outer-sphere reorganization (λ_o) energy. The value of λ_i is always small and $\lambda = \lambda_o + \lambda_i = \lambda_o$. The value of λ_o can be estimated from the physical properties of the solvent and geometry of the reactants (eq.11),

$$\lambda_o = e^2(1/2r_a+1/2r_b-1/d)\ (1/D_{op}-1/D_s) \quad (11)$$

where e is the electronic charge, D_{op} and D_s are optical and static dielectric constants of the medium, r_a and r_b are the radii of the reactants and $d=r_a+r_b$. The radii of Mn^{V} complex and sulphide are taken as 7.8 and 4.0 Å respectively.[60] Substitution of eq.(10) in the expression from transition state theory ,eq.(12)

$$k_{et} = \nu_n \exp[-\Delta G^{\ddagger}/RT] \quad (12)$$

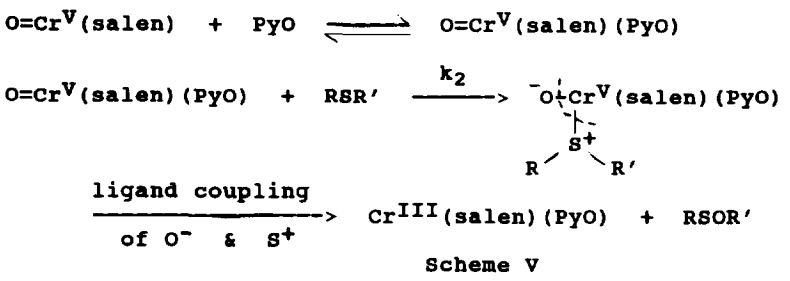
gives an expression for k_{et} in terms of ΔG (eq.12).

$$k_{et} = \nu_n \exp[-\lambda(1+\Delta G/\lambda)^2/4RT] \quad (13)$$

In this equation, ν_n is the nuclear frequency and can be taken as $1\times10^{11}\ M^{-1}s^{-1}$. Since experimental rate constants, k_2 (k_{et}), and λ are

known, the value of ΔG can be calculated from eq. (13). Using this value of ΔG in eq.(9), $E_{Mn^{V}/Mn^{IV}}$ values for the six oxomanganese(V) complexes are estimated and are given in Table 3. The reduction potential values of $O{=}Mn^{V}$ complexes are higher than those of $Cr^{V}{=}O$ complexes[18] (Table 3) and therefore the former are more reactive towards sulphides than the latter.

III. Comparison with Cr(V) Oxidation of Organic Sulphides. Recently we have investigated the oxochromium(V) oxidation of organic sulphides[55] and the reaction follows simple second-order kinetics, first-order in each reactant. To account for the kinetic results, a mechanism involving the rate-determining nucleophilic attack of sulphide on Cr centre of the complex followed by ligand coupling between sulphide and O^{-} to form sulphoxide has been proposed. This redox reaction is efficiently catalysed by donor ligand,pyridine N-oxide (PyO) and the catalysis is explained in terms of the formation of more reactive Cr(V)-donor adduct (Scheme V). The catalytic activity of PyO in the Mn^{V} oxidation of sulphides is small (Table 2). Thus the behaviour of $Cr^{V}{=}O$ and $Mn^{V}{=}O$ complexes towards sulphides is very similar to their reactions with alkenes.[18,19] Thus to account for different behaviour of $Cr^{V}{=}O$ and $Mn^{V}{=}O$ complexes towards sulphides different mechanisms have been proposed.



Scheme V

Conclusion. Six oxo(salen)manganese(V) complexes have been generated *in situ* in acetonitrile and the oxidizing capability of the oxo complexes has been studied with several aryl methyl and dialkyl sulphides in acetonitrile at 25°C. The sulphides are converted selectively to sulphoxides. Electronic-substrate and electronic-oxidant effects on the reaction have been analysed. A mechanism involving single electron transfer in the rate-determining step has been proposed for the oxygen atom transfer from oxo(salen)manganese(V) complex to sulphide. The possibility of electrophilic attack of Mn on the sulphide sulphur has also been discussed. The reduction potential values of all the six complexes have been estimated using Marcus equation. Finally, a comparison between the reactivity of $Cr^{V}{=}O$ and $Mn^{V}{=}O$ complexes towards sulphides has been made.

Acknowledgement

Financial assistance for this work in the form of a project from Council of Scientific and Industrial Research, New Delhi, is gratefully acknowledged.

References

1. Sheldon, R.A.; Kochi, J.K. *Metal Catalysed Oxidation of Organic Compounds*; Academic Press: New York, 1981; Drago, R.S.; *Coord. Chem. Rev.* **1992**, 117, 185; Jorgensen, K.A. *Chem. Rev.* **1989**, 89, 431; Holm, R.H. *Coord.Chem.Rev.* **1990**, 100, 183.

2. Meunier, B. *Chem. Rev.* **1992**, 92, 1411; Holm, R.H. *Chem. Rev.* **1987**, 87, 1401.

3. Curci, R.; Giannattasio, S.; Sciacovelli, O.; Troisi, L. *Tetrahedron* **1984**, 40, 2763.

4. Groves, J.T.; Nemo, T.E. *J. Am. Chem. Soc.* **1983**, 105, 5786; Groves, J.T.; Subramanian, D.V. *J.Am.Chem.Soc.* **1984**, 106, 2177.

5. Chang, C.K.; Kuo, M-S. *J. Am. Chem. Soc.* **1979**, 101, 3413; Traylor, P.S.; Dolphin, D.; Traylor, T.G. *J.Chem.Soc.,Chem.Commun.* **1984**, 279.

6. Smegal, J.A.; Schardt, B.C.; Hill, C.L. *J. Am. Chem. Soc.* **1983**, 105, 3510; Smegal, J.A.; Hill, C.L. *J.Am.Chem.Soc.* **1983**, 105, 3515.

7. Groves, J.T.; Haushalter, R.C.; Nakamura, M.; Nemo, T.E.; Evans,B.J. *J.Am.Chem.Soc.* **1981**, 103, 2884; Mansuy, D.; Bortoli, J.F.; Momenteau, M. *Tetrahedron Lett.* **1982**, 23, 2781.

8. Oae, S.; Watanabe, Y.; Fujimori, K. *Tetrahedron Lett.* **1982**,23,1189; Vassel, K.A.; Espenson, J.H. *Inorg.Chem.* **1994**, 33, 5491.

9. Guilmet, E.; Meunier, B. *Tetrahedron Lett.* **1980**, 21,4449; Guilmet,E.; Meunier, B. *Tetrahedron Lett.* **1982**, 23, 2449.

10. Nee, A.W.; Bruice, T.C. *J.Am.Chem.Soc.* **1982**, 104, 6123; Dicken, C.M.; Lu, F-L.; Nee, M.W.; Bruice, T.C. *J.Am.Chem.Soc.* **1985**, 107, 5776.

11. Powell, M.F.; Pai, E.F.; Bruice, T.C. *J.Am.Chem.Soc.* **1984**, 106, 3277.

12. Takata,T.; Tajima,R.; Ando,W. *Phosphorous,Sulfur Silicon* **1983**, 16,67.

13. Acquaye, J.H.; Muller, J.G.; Takeuchi, K.J. *Inorg.Chem.* **1993**, 32,160.

14. Dufour, M.N.; Crumbliss, A.L.; Johnston, G.; Gaudemer,A. *J.Mol.Catal.* **1980**, 7, 277.

15. Traylor, T.G.; Miksztal, A.R.; *J. Am. Chem. Soc.* **1987**, 109, 2770; Castellino, A.J.; Bruice, T.C. *J.Am.Chem.Soc.* **1988**, 110, 158.

16. Groves, J.T.; Watanabe, Y. *J.Am.Chem.Soc.* **1986**,108,507; Collman,J.P.; Kodadek, J.P.; Raybuck, S.A.; Brauman, J.I.; Papazian, L.M. *J. Am. Chem.Soc.* **1985**, 107, 4343.

17. Groves, J.T.; Stern, M.K. *J. Am. Chem. Soc.* **1988**, 110, 8628.

18. Srinivasan, K.; Kochi, J.K. *Inorg.Chem.* **1985**, 24, 4671; Samsel, E.G.; Srinivasan, K.; Kochi, J.K. *J.Am.Chem.Soc.* **1985**, 107, 7606.

19. Srinivasan, K.; Michaud, P.; Kochi,J.K. *J.Am.Chem.Soc.* **1986**,108,2309.

20. Righter, B.; SriHari, S.; Hunter, S.; Masnovi, J. *J. Am. Chem. Soc.* **1993**, 115, 3918.

21. Khan,M.M.T.;Chatterjee,D.;Merchant,R.R.;Paul,P.;Abdi,S.H.A.;Srinivas, D.; Siddiqui, M.R.H.; Moiz,M.A.; Bhadbhade, M.M.; Venketasubramanian, K. *Inorg.Chem.* **1992**, 31, 2711.

22. Gelb, M.H.; Toscano, W.A.,Jr.; Sligar, S.C. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, 79, 5758.

23. Amesz, J. *Biochim.Biophys.Acta.* **1983**, 726,1; Pecoraro,V.L. *Photochem. photobiol.* **1988**, 48, 249.

24. Ludwig, M.; Pattridge, K.A.; Stallings, W.C. *Manganese in Metabolism and Enzyme Function*; Academic Press: New York, 1986, Chapter 21,p405; Beyer, W.,Jr.; Froderich, I. *Manganese in Metabolism and Enzyme Function*; Academic Press: New York, 1986, Chapter 12, p193.

25. Groves, J.T.; Stern, M.K. *J.Am.Chem.Soc.* **1988**, 110,8628; Anelli,P.L.; Banfi, S.; Montanari, F.; Quici, S. *J.Chem.Soc., Chem.Commun.* **1989**, 779; Perzee-Fauvet,M.; Gaudemer,A. *J.Chem.Soc.,Chem.Commun.* **1981**,874.

26. Oae, S. *In Organic Chemistry of Sulfur*; Plenum Press: New York, 1977; Block, E. *In Reactions of Organosulfur Compounds*; Academic Press: New York, 1978.

27. Shen, C.; Foote, C.S.; Gu, C.L. *J.Am.Chem.Soc.* **1992**, 114, 3015 and references cited therein.

28. Sato, R.; Omuru, Y. *Cytochrome P-450*; Kodansha, Tokyo and Academic Press: New York, 1978.

29. Zahn, H.; Zuber, H. *Chem.Ber.* **1953**, 86, 180.

30. Burton, H.; Hu, P.F. *J.Chem.Soc.* **1948**,603; Baliah,V.;Shunmughanathan, Sp.; Varadachari, R. *J.Phys.Chem.* **1957**, 61, 1013.

31. Baliah, V.; Uma, M. *Tetrahedron* **1963**, 19, 455.

32. Pfeiffer,P.; Breith,E.; Lubbe,E.;Tsumaki,T. *Leibigs.Ann.* **1933**,503,84.

33. Charlesworth, E.H.; Charleson, P. *Can.J.Chem.* **1968**, 46, 1843.

34. Saltzman, H.; Sharefkin,J.G. *Organic Syntheses*; Wiley: New York,1973; Collect. Vol. V,p658.

35. Perrin, D.D.; Armarego, W.L.; Perrin, D.R. *Purification of Laboratory Chemicals*; Pergamon Press: New York, 1980.

36. Srinivasan, C.; Kuthalingam, P.; Arumugam, N. *J. Chem. Soc., Perkin Trans.2* **1980**, 170.

37. Carnieri, N.; Harriman, A.; Porter,G. *J.Chem.Soc.,Dalton Trans.* **1982**, 931; Carniery, N.; Harriman,A.; Porter,G.; Kalyanasundaram, K.*J.Chem. Soc.,Dalton Trans.* **1982**, 1231.

38. Johnson,C.D. *Hammett Equation*; Cambridge University: New York, 1980.

39. Bernardi, F.; Distefano, G.; Mangini, A.; Pignataro, S.; Spunta, S. *J.Electron Spectrosc.Relat.Phenom.* **1975**, 7, 457;Watanabe,Y.;Iyanagi, T.; Oae,S. *Tetrahedron Lett.* **1980**,21,3685; Ando,W. *Sulfur Rep.* **1981**, 1, 147.

40. Watabe, T.; Akamatsu, K. *Biochem.Pharmacol.* **1974**, 23, 1079; Hanzilk, R.P.; Shearer, G.O. *Biochem.Pharmacol.* **1971**, 20, 912.

41. Pryor, W.A.; Hendrichson, W.H.,Jr., *J.Am.Chem.Soc.* **1983**, 105, 7114.

42. Miller, A.E.; Bischoff, J.J.; Bizub, C.; Luminoso, P.; Smiley, S. *J.Am.Chem.Soc.* **1986**, 108, 7773.

43. Srinivasan, C.; Chellamani,A.; Rajagopal,S. *J.Org.Chem.* **1985**,50,1201.

44. Baciocchi, E.; Intini, D.; Piermattei, A.; Roh, C.; Ruzziconi, R. *Gazz.Chim.Ital.* **1989**, 119, 649.

45. Arumugam, N.; Srinivasan, C.; Kuthalingam, P. *Indian J. Chem., Sect.A*, **1978**, 16, 478; Srinivasan,C.; Kuthalingam,P.; Arumugam,N. *Can.J.Chem.* **1978**, 56, 3043; Srinivasan, C.; Kuthalingam, P.; Arumugam, N. *J.Chem. Soc.,Perkin Trans.2* **1980**, 170.

46. Arocoria,A.; Ballistreri, F.P.;Spina, E.;Tomaselli,G.A.;Toscano, R.M. *Gazz.Chim.Ital.* **1990**, 120, 309.

47. Davis, F.A.; McCanley, J.P.; Chattopachayay, S.; Herakai, M.; Towson, J.C.; Watson, W.H.; Taranaiepour, R. *J.Am.Chem.Soc.* **1987**, 109, 3370.

48. Srinivasan,C.; Chellamani,A.; Kuthalingam,P. *J.Org.Chem.* **1982**,47,428.

49. Rajasekeran,K.;Baskaran,T.;Gnanasekaran,C. *J.Chem.Soc.,Perkin Trans.2* **1984**, 1183.

50. Lee, D.G.; Chen, T. *J.Org.Chem.* **1991**, 53, 5346.

51. Groves, J.T.; Kruper, W.J.,Jr. *J.Am.Chem.Soc.* **1979**, 101,7613; Groves, J.T.; Watanabe, Y.; McMurry, T.C. *J.Am.Chem.Soc.* **1983**, 105, 4489.

52. Silvarman, J.; Dodson, R.W. *J.Phys.Chem.* **1952**, 56, 846.

53. Watanabe, Y.; Numata, T.; Iyanagi,T.; Oae,S. *Bull.Chem.Soc.Jpn.* **1981**, 54, 1163.

54. Balakumar,S.; Rajagopal,S.; Thanasekaran, P.; Ramaraj, R. *Tetrahedron* **1995**, 51, 4801.

55. Sevvel,R.; Rajagopal,S.; Srinivasan, C.; Alhaji, N.M.I.; Chellamani, A. *J.Mol.Catal.* (Submitted).

56. Srinivasan,C.; Rajagopal,S.; Chellamani,A. *J.Chem.Soc.,Perkin Trans.2* **1990**, 1839.

57. Roh, K.R.; Kim, K.S.; Kim, Y.H. *Tetrahedron Lett.* **1991**, 32, 793.

58. Oae, S.; Uchida, Y. *Acc.Chem.Res.* **1991**, 24, 202.

59. Marcus,R.A.; Sutin,N. *Biochim.Biophys.Acta.* **1985**, 811, 265; Sutin, N. *Prog.Inorg.Chem.* **1983**, 30, 441.

60. Srinivasan, K.; Kochi, J.K. *Inorg. Chem.* **1985**, 24, 4674; Gnanaraj, G.A.; Rajagopal, S.; Srinivasan, C.; Pitchumani, K. *Tedrahedron* **1983**, 49,4721.

(*Received in UK* 24 *July* 1995; *accepted* 28 *September* 1995)