

Kinetics and Mechanism of (salen)Mn^{III} Catalyzed Oxidation of Aryl phenyl Sulfides with Sodium Metaperiodate

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Abstract

The oxidation of 4-substituted phenyl phenyl sulfides was carried out with several oxo(salen)manganese(V) complexes in MeCN/H₂O 9:1. The oxidation follows an overall second-order kinetics, first-order each in sulfide and oxo(salen)manganese(V) complex. Electron-attracting substituents in the sulfide and electron-releasing substituents in salen of the oxo(salen)manganese(V) complexes reduce the rate of oxidation. A Hammett analysis of the rate constants for the oxidation of 4-substituted phenyl phenyl sulfides gives a negative ρ value ($\rho = -2.29$) indicating an electron-deficient transition state. The log k_2 value observed in the oxidation of each 4-substituted phenyl phenyl sulfides by substituted oxo(salen)manganese(V) complexes also correlate with Hammett σ constants, giving positive ρ value. The substituent-, acid-, and solvent-effect studies indicate direct O-atom transfer from the oxidant to the substrate in the rate-determining step.

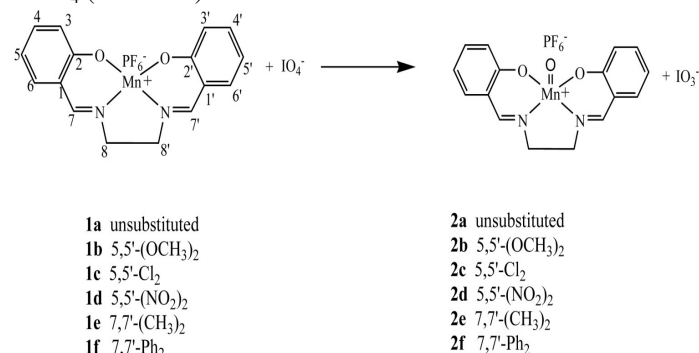
Keywords: Organic sulfides, sodium metaperiodate, (salen) Mn^{III} complexes, catalyzed oxidation, reaction mechanism.

Introduction

The periodate oxidation is undoubtedly one of the most widely used reactions in organic chemistry^{1,2}. Transition metal complexes with Schiff base and porphyrin ligands have been extensively used as models for the heme containing cytochrome P-450³. As biomimetic models, transition metal Schiff base complexes have been found to be good catalysts in a variety of oxygenation reactions including epoxidation of olefins and the hydroxylation of alkenes³. Many efficient biomimetic oxidation systems using iron and manganese porphyrins as catalysts, and various single oxygen atom donors, such as PhIO, ClO⁻, H₂O₂, ROOH or IO₄⁻ have been reported^{4,6}.

Organic sulfides, which are strong nucleophiles, are oxidized to sulfoxides exclusively by electrophilic oxygen transfer reagents^{7,8}. Mirkhani and co-workers⁹ studied the (salen)Mn^{III}-catalyzed oxidation of sulfides, primary aromatic amines, alkene epoxidation and oxidative decarboxylation with NaIO₄. Mohajer and co-workers¹⁰ reported that sodium periodate can efficiently epoxidize various alkenes in the presence of chlorotetra-phenylporphyrinatomanganese(III). The periodate oxidation of sulfides to sulfoxides under mild conditions is widely used in syntheses¹¹. Ruff and co-workers studied the oxidation of sulfides with sodium periodate in the absence of catalyst¹². Recently, Chellamani et al, reported the results on the [Mn^{III}(salen)]-catalyzed NaOCl and PhIO oxidation of organic sulfides and sulfoxides¹³. A survey of the literature showed that there are only a few reports on the oxidation of organic sulfides with NaIO₄⁹⁻¹² and there is no report on the mechanistic study of metal complexes catalyzed oxidation of organic sulfides with NaIO₄. In this paper, we report the kinetics and mechanism of the oxidation of aryl phenyl sulfides with NaIO₄ catalyzed by (salen)Mn^{III} complexes 1a-1f.

The active species in the present reaction is considered to be the oxo(salen)manganese(V) complex, as proposed by Mirkhani and co-workers⁹ and others¹⁰ in the (salen)Mn^{III}-catalyzed NaIO₄ oxidation of achiral derivatives. The oxo(salen)manganese(V) complexes 2a-2f are generated in situ from the corresponding [(salen)Mn^{III}]⁺PF₆⁻ complexes and NaIO₄ (scheme 1).



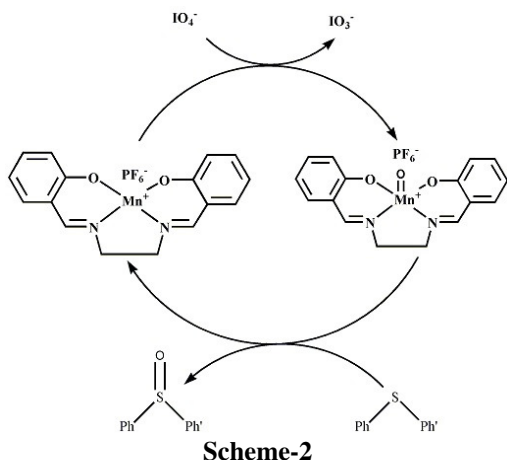
Scheme-1

Material and Method

Materials: Sodium metaperiodate purchased from Aldrich was used as such. Acetonitrile (GR, Merck) was first refluxed over P₂O₅ for 5h and then distilled. Diphenyl sulfide (DPS), para-substituted aryl phenyl sulfides were prepared by known methods¹³. The [(salen)Mn^{III}]⁺PF₆⁻ complexes **1a-1f** were synthesized according to reported procedures^{13,14}.

Kinetic measurements: The oxo(salen)manganese(V) complexes 2a-2f were obtained by mixing equimolar quantities of (salen)Mn^{III} complex and sodium periodate (scheme 2). The solutions were prepared freshly for each kinetic run. The kinetic

measurements were carried out in 90%CH₃CN-10%H₂O at 20±0.1°C under pseudo-first-order conditions using 20-100 fold excess of the substrate in a Perkin-Elmer UV-visible spectrophotometer (Lambda 25) fitted with thermo-stated 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 5ml. The progress of the reaction was monitored by following the decay of oxo complex at 680nm. The rate constants were evaluated from slopes of linear plots of log(A_t-A_∞) vs. time, where A_t is the absorbance at time and A_∞ is the experimentally determined infinity point. The values of k₁ were obtained from k₁=k_{1(obs)}-k_{1(dec)}. Where k_{1(obs)} is the pseudo-first-order rate constants in the presence of sulfide and k_{1(dec)} is the self-decomposition rate constants of oxo(salen)manganese(V) complexes. The second-order rate constants were obtained from k₂=k₁/[sulfide].



Data analysis: Data analysis was performed using Microcal Origin (version 6.0) computer software. The goodness of the fit is discussed using the correlation coefficients and standard deviations.

Results and Discussion

Stoichiometry and reaction product: The stoichiometry of the reaction between the (salen)Mn^V=O complex and sulfide was studied under the experimental conditions [2a] = 0.0028M and [PhSPh] = 0.20M. Gas chromatographic analysis of the samples showed that the yield of sulfoxides is 72% and that of Mn^{III} complex is 95% with negligible amount of sulfone. In view of that, the stoichiometry of the reaction can be represented by equation 1.



Effect of reactant concentrations: At constant initial concentration of DPS, constant values of k₁ were obtained upon varying the initial concentration of 2a table-1, this, coupled with the observation of linear log (A_t-A_∞) versus time plots (r >

0.994), ensures that the order in 2a is one. The unit slope observed from log-log plots of k₁ and [DPS]₀ (figure 1; r > 0.996) and the linear plots of k₁ versus [sulfide]₀ which pass through origin (figure 2; r > 0.996) establish that the reaction is first-order in sulfide. Hence, the reaction is overall second-order, first-order in each reactant. Therefore the rate law can be given by equation 2.

$$(-d[2])/dt = k_2[2][sulfide] \quad (2)$$

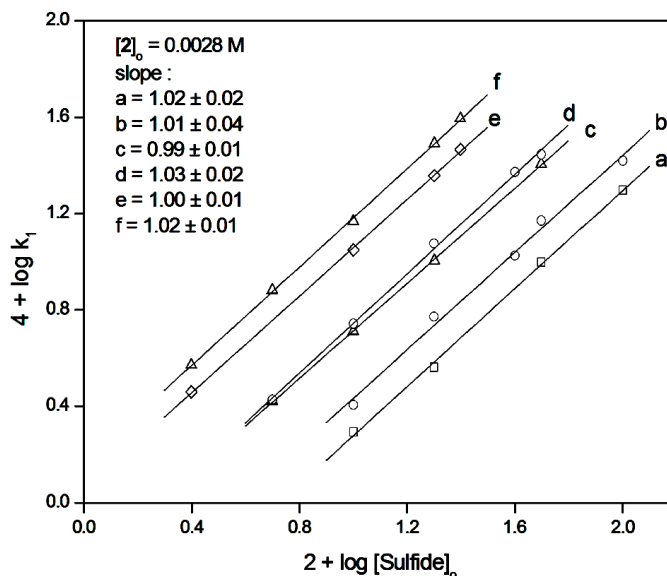


Figure-1
Double log plots of k₁ and [DPS]₀

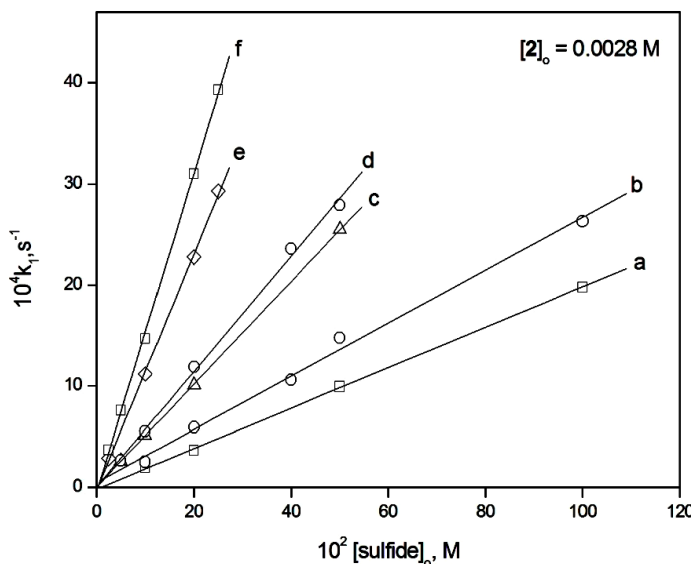


Figure-2
Plots of k₁ vs. [sulfide]₀ for the oxidation of a) DPS with 2b, b) DPS with 2a, c) DPS with 2c, d) 4-MeC₆H₅SPh with 2a, e) DPS with 2d, and f) 4-MeOC₆H₅SPh with 2a

Effect of pyridine N-oxide (pyo): The effect of PyO on the reaction rate has been studied and the rate data are listed in table-2. The rate of the reaction is not affected appreciably by the addition of PyO. This indicates that PyO is not binding with oxo(salen)manganese(V) complex and has no catalytic effect during the oxidation process^{6,15}. Similar results are observed in the (salen)MnIII-catalyzed reactions¹³.

Effect of trichloroacetic acid and solvent composition: To understand the effect of acid and solvent composition on the kinetics of this reaction, the rates at different concentrations of trichloroacetic acid and solvent composition were measured, and the data are collected in table-3. The rate data show that the increase in [acid] as well as the increase in the polarity of the medium favors the rate of oxidation.

Effect of substituents: The effect of substituents present at the 4-position of the substituted phenyl phenyl sulfides on the reaction rate has been studied and the rate data presented in table-4. Electron-attracting substituents in the phenyl ring retard the rate while electron-releasing substituents produce the opposite effect. The $\log k_2$ values are better correlated with σ_p constants (figure 3; $r = 0.997$, $\rho = -2.29 \pm 0.09$, $s = 0.077$) than with σ^+/σ^- constants (figure 4; $r = 0.990$, $\rho = -1.27 \pm 0.11$, $s = 0.164$). The negative ρ value indicates an accumulation of positive charge at S-atom, and the magnitude of the ρ value indicate the extent of charge development at the S-atom in the transition state of the rate-limiting step¹⁶.

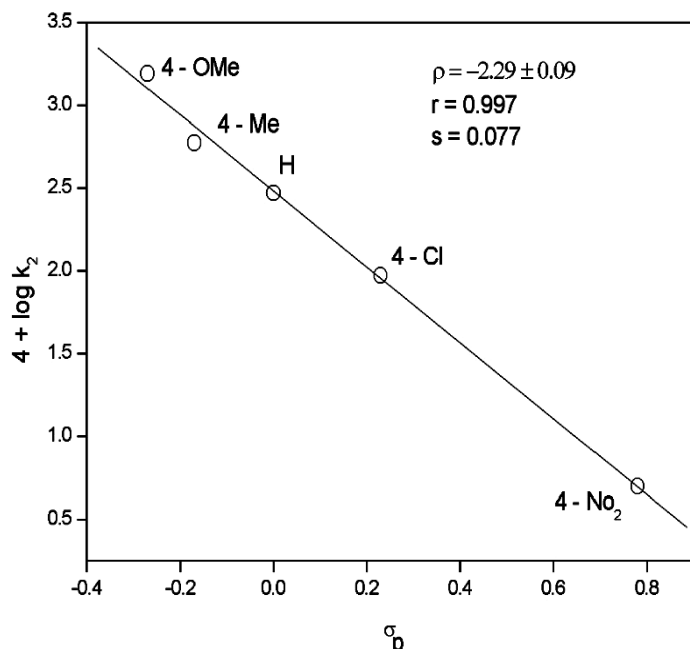


Figure-3
Hammett plot for the oxidation of 4-substituted phenyl phenyl sulfides by 2a

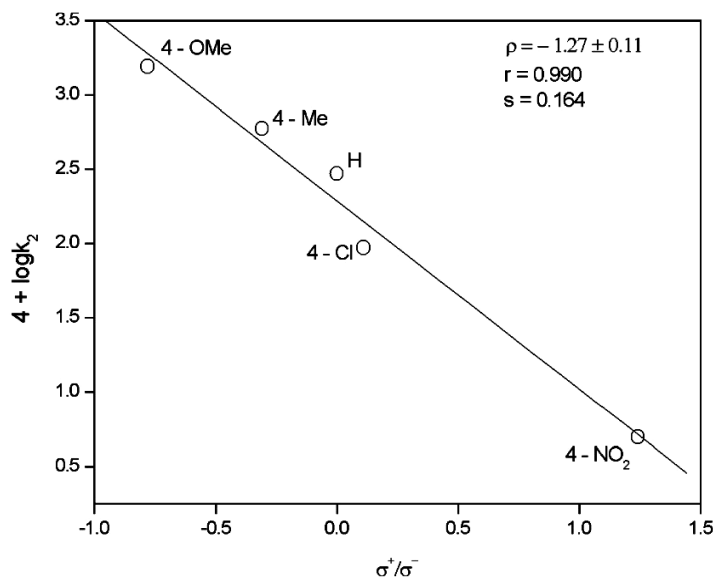


Figure-4
Hammett plot for the oxidation of 4-substituted phenyl phenyl sulfides by 2a

The effect of changes in the electronic nature of the oxidant on the rate of oxidation of the 4-substituted phenyl phenyl sulfides with oxo(salen)manganese(V) complexes **2a-2d**, and the second-order rate constants are included in table-4. It is seen that electron-releasing substituents at the 5,5'-positions of salen ligand retard the rate while electron-withdrawing substituents accelerate it. Hammett correlation of $\log k_2$ with $2\sigma_p$ is excellent with the ρ value of 0.38 ± 0.02 (figure 5; $r = 0.996$, $s = 0.038$). The positive ρ value indicates the build-up of negative charge at the metal centre in the transition state of the rate-determining step.

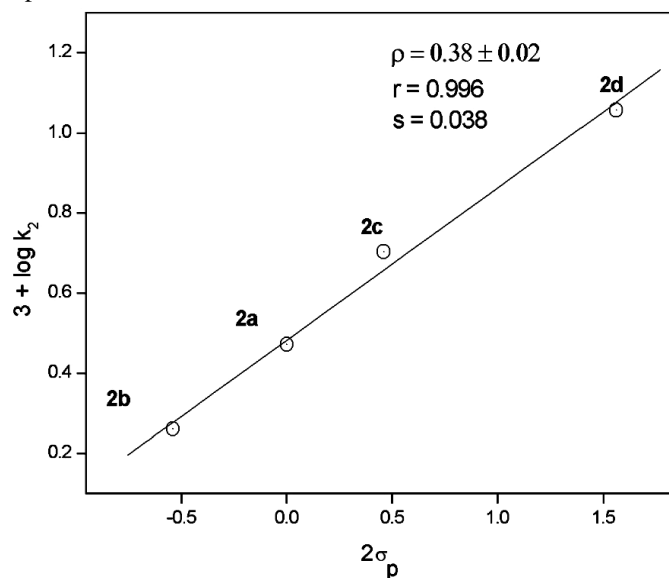


Figure-5
Hammett plot for the oxidation of DPS by substituted oxo(salen)manganese(V) complex

Table-1
Rate constants for the oxidation of DPS by 2a-f in 90 % acetonitrile-10% water(v/v) mixture at 20°C^a

$10^2[\text{DPS}]_0, \text{M}$	$10^3[2]_0, \text{M}$	$10^4 k_{1(\text{obs})}, \text{s}^{-1}$ ^b	$10^4 k_{1(\text{dec})}, \text{s}^{-1}$ ^c	$10^4 k_1, \text{s}^{-1}$ ^d	$10^3 k_2, \text{M}^{-1} \text{s}^{-1}$ ^e
-	2a	-	-	-	-
10.0	1.60	8.25±0.16	5.52±0.05	2.73±0.11	2.73±0.11
10.0	1.80	8.42±0.22	5.49±0.07	2.93±0.15	2.93±0.15
10.0	2.00	8.02±0.09	5.56±0.03	2.46±0.06	2.46±0.06
10.0	2.50	8.16±0.29	5.61±0.04	2.55±0.25	2.55±0.25
10.0	2.80	8.32±0.12	5.78±0.06	2.54±0.06	2.54±0.06
10.0	3.00	8.12±0.15	5.77±0.05	2.35±0.10	2.35±0.10
20.0	2.80	11.7±0.12	5.78±0.06	5.92±0.06	2.96±0.03
40.0	2.80	16.4±0.42	5.78±0.06	10.6±0.36	2.66±0.09
50.0	2.80	20.6±0.46	5.78±0.06	14.8±0.40	2.96±0.08
100.0	2.80	32.1±0.86	5.78±0.06	26.3±0.80	2.63±0.08
-	2b	-	-	-	-
10.0	2.80	6.81±0.21	4.85±0.03	1.96±0.18	1.96±0.18
20.0	2.80	8.49±0.15	4.85±0.03	3.64±0.12	1.82±0.06
50.0	2.80	14.8±0.38	4.85±0.03	9.95±0.35	1.99±0.07
100.0	2.80	24.6±0.72	4.85±0.03	19.8±0.69	1.98±0.07
-	2c	-	-	-	-
5.0	2.80	8.28±0.36	5.65±0.05	2.63±0.31	5.26±0.06
10.0	2.80	10.8±0.16	5.65±0.05	5.15±0.11	5.15±0.11
20.0	2.80	15.7±0.38	5.65±0.05	10.1±0.33	5.05±0.02
50.0	2.80	31.1±0.72	5.65±0.05	25.5±0.67	5.10±0.01
-	2d	-	-	-	-
2.5	2.80	9.00±0.12	6.12±0.05	2.88±0.07	11.5±0.03
10.0	2.80	17.3±0.45	6.12±0.05	11.2±0.40	11.2±0.40
20.0	2.80	28.9±0.87	6.12±0.05	22.8±0.82	11.4±0.41
25.0	2.80	35.4±1.02	6.12±0.05	29.3±0.97	11.7±0.39
-	2e	-	-	-	-
10.0	2.80	8.23±0.15	5.63±0.06	2.60±0.09	2.60±0.09
20.0	2.80	10.2±0.54	5.63±0.06	4.57±0.48	2.29±0.24
50.0	2.80	17.8±0.92	5.63±0.06	12.2±0.86	2.44±0.17
100.0	2.80	28.9±1.02	5.63±0.06	23.3±0.96	2.33±0.96
-	2f	-	-	-	-
10.0	2.80	7.89±0.23	5.56±0.08	2.33±0.15	2.33±0.15
20.0	2.80	9.83±0.48	5.56±0.08	4.27±0.42	2.13±0.21
50.0	2.80	16.8±0.69	5.56±0.08	11.2±0.61	2.24±0.01
100.0	2.80	26.3±1.02	5.56±0.08	20.7±0.94	2.07±0.94

^aAs determined by a spectrophotometric technique following the disappearance of oxomanganese(V) at 680nm; the error quoted in k values is the 95% confidence limit of *Student's t-test*. ^bEstimated from pseudo-first-order plots over 40-45% reaction. ^cEstimated from first-order plots over 50-60% reaction in the absence of sulfide. ^dObtained as $k_1 = k_{1(\text{obs})} - k_{1(\text{dec})}$. ^eIndividual k_2 values estimated as $k_1/[\text{DPS}]_0$.

Table-2
Effect of pyridine N-Oxide on the rate of oxidation of DPS by 2a (0.0028 M) in 90 % acetonitrile-10% water (v/v) mixture at 20°C^a

$10^2[\text{DPS}]_0, \text{M}$	$10^2[\text{PyO}]_0, \text{M}$	$10^4 k_{1(\text{obs})}, \text{s}^{-1}$ ^b	$10^4 k_{1(\text{dec})}, \text{s}^{-1}$ ^c	$10^4 k_1, \text{s}^{-1}$ ^d	$10^3 k_2, \text{M}^{-1} \text{s}^{-1}$ ^e
10.0	0.0	8.32±0.12	5.78±0.06	2.54±0.06	2.54±0.06
10.0	2.5	8.35±0.21	5.54±0.05	2.81±0.16	2.81±0.16
10.0	5.0	8.62±0.23	5.38±0.08	2.74±0.17	2.74±0.17
10.0	10.0	8.23±0.16	5.50±0.07	2.73±0.10	2.73±0.10
10.0	20.0	8.72±0.35	5.79±0.06	2.93±0.29	2.93±0.29
10.0	25.0	8.64±0.19	5.62±0.06	3.02±0.13	3.02±0.13

^aAs determined by a spectrophotometric technique following the disappearance of oxomanganese(V) at 680nm; the error quoted in k values is the 95% confidence limit of *Student's t-test*. ^bEstimated from pseudo-first-order plots over 40-45% reaction. ^cEstimated from first-order plots over 50-60% reaction in the absence of sulfide. ^dObtained as $k_1 = k_{1(\text{obs})} - k_{1(\text{dec})}$. ^eIndividual k_2 values estimated as $k_1/[\text{DPS}]_0$.

Table-3
Effect of adding acid and changing the solvent composition on the rate of oxidation of DPS by 2a at 20°C^{a,b}

$10^3[\text{Acid}]^c, \text{M}$	$10_4 k_1, \text{d}^d, \text{s}^{-1}$	$\text{CH}_3\text{CN}\%-\text{H}_2\text{O}\% (\text{v/v})$	$10_4 k_1, \text{e}^e, \text{s}^{-1}$
0.0	2.54±0.06	90:10	5.92±0.06
0.5	3.65±0.22	85:15	9.02±0.45
1.0	6.61±0.20	80:20	12.2±0.27
5.0	25.6±0.59	75:25	15.7±0.64
10.0	43.7±1.70	70:30	18.4±1.04
20.0	99.3±3.6	-	-

^aGeneral conditions: $[\mathbf{2a}]_0 = 0.0028 \text{ M}$. ^bIn the evaluation of rate constants, the self-decomposition of 2a at different [acid] and solvent composition taken into account. ^c CCl_3COOH . ^d $[\text{DPS}]_0 = 0.10 \text{ M}$; Solvent: 90% CH_3CN – 10% H_2O (v/v), ^e $[\text{DPS}]_0 = 0.20 \text{ M}$.

Table-4
Second-order rate constants for ρ value for the reactions of 4-XC₆H₄SPh with 2a-d in 90% acetonitrile-10% water(v/v) mixture at 20°C^{a,b}

X	Oxo(salen)manganese(V) complex $10^3 k_2, \text{M}^{-1} \text{s}^{-1}$				ρ^d	(r)
	2b	2a	2c	2d		
OMe	9.55±0.48	15.5±0.35	24.6±0.80	35.4±0.97	0.266±0.05	(0.963)
Me	3.47±0.03	5.95±0.11	10.7±0.40	18.6±0.88	0.345±0.05	(0.977)
H	1.82±0.06	2.96±0.03	5.05±0.02	11.4±0.41	0.380±0.02	(0.996)
Cl	0.62±0.12	0.94±0.10	2.13±0.03	3.29±0.12	0.353±0.07	(0.957)
NO_2^c	0.03±0.02	0.05±0.02	0.08±0.02	0.13±0.01	0.299±0.04	(0.977)
ρ^e	-2.29±0.11	-2.29±0.09	-2.29±0.12	-2.30±0.11	-	-
(r)	(0.997)	(0.997)	(0.996)	(0.996)	-	-

^aThe error quoted in k_2 is the 95% confidence limit of Student's *t*-test. ^bGeneral conditions: $[\mathbf{2}]_0 = 0.0028 \text{ M}$; $[\text{sulfide}]_0 = 0.50 \text{ M}$. ^dThe ρ values were obtained by correlating $\log k_2$ with $2\rho_p$ for the reaction of various oxo(salen)manganese(V) complexes with a given sulfide. ^eThe ρ values were obtained by correlating $\log k_2$ with σ_p for the reaction of various sulfides with a given oxo(salen)manganese(V) complex.

Table-5
Second-order rate constants and activation parameters for the oxidation of p-XC₆H₄SPh by 2a in 90% acetonitrile-10% water(v/v) mixture at four different temperatures.^a

X	$10^3 \cdot k_2 [\text{M}^{-1} \text{s}^{-1}]$				ΔH^\ddagger [kJ mol ⁻¹]	$-\Delta S^\ddagger$ [JK ⁻¹ mol ⁻¹]	ΔG^\ddagger [kJ mol ⁻¹] ^d
	293K	298K	303K	313K			
OMe ^b	14.7±0.22	21.4±0.91	29.4±1.35	58.4±2.22	49.8	141	92.5
Me	5.95±0.11	9.25±0.42	11.9±0.46	23.0±0.95	47.9	279	132.5
H	2.54±0.06	3.82±0.23	5.65±0.17	10.8±0.27	52.6	191	110.5
Cl	0.94±0.10	1.57±0.11	2.18±0.18	4.60±0.59	56.9	124	94.5
NO_2^c	0.05±0.02	0.15±0.01	0.21±0.06	0.70±0.20	93.3	72.9	115.4

^aGeneral condition: $[\mathbf{2a}]_0 = 0.0028 \text{ M}$; $[\text{sulfide}]_0 = 0.20 \text{ M}$, unless otherwise noted. ^b $[\text{sulfide}]_0 = 0.10 \text{ M}$. ^c $[\text{sulfide}]_0 = 0.50 \text{ M}$. ^dat 303K

The effect of substituents at the 7,7'-positions of the salen ligand of oxo(salen)manganese(V) complexes on the reaction rate was studied with **2a**, **2e**, and **2f** for the oxidation of DPS. The rate data in Table-1 show that the presence of Me or Ph groups at the 7,7'-positions slightly reduces the rate.

Effect of temperature: The oxo(salen)manganese(V) oxidation of para-substituted phenyl phenyl 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-5.

Mechanism of oxidation: Oxygen atom transfer to organic substrates has been proposed to proceed by two different

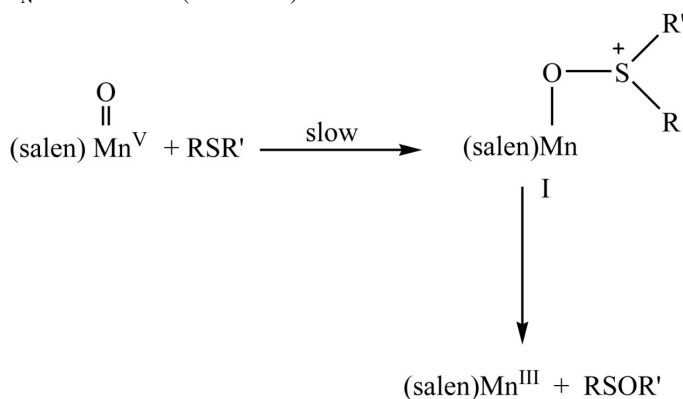
mechanisms. The oxidants such as Cr(VI)¹⁶, Ce(IV)¹⁷ and Fe(III)-polypyridyl complexes¹⁴ oxidize sulfides by SET mechanism. Oxidation of sulfides with (salen)Mn^{III}-catalyzed NaOCl¹³ follow a S_N2 mechanism. The observation of overall second-order kinetics, first-order each in oxo complex and sulfide, indicates that the present reaction follows simple kinetics without involving any complex mechanism.

The Hammett equation has been used to analyze the oxidation of sulfides to sulfoxides. In the present study, a low ρ value of -1.27 is obtained. The size of the ρ value cannot be taken as evidence for the operation of a SET or S_N2 mechanism in a particular reaction¹⁹. For example, it has been argued that a low ρ value for the oxidation of aryl methyl sulfides by Cr(VI) ($\rho = -$

2.07)¹⁶, Ce(IV) ($\rho = -3.3$)¹⁷ and Fe(III)-polypyridyl complexes ($\rho = -3.2$)¹⁴ indicates SET mechanism and that a low ρ value for the oxidation of sulfides with sodium periodate (-1.40)¹² and (salen)MnIII-catalyzed NaOCl ($\rho = -1.85$)¹⁴ indicates S_N2 mechanism. Reactions that involve rate-limiting single electron transfer from sulfur to yield radical cation intermediates are known to give better Hammett correlations when σ^+ substituent constants are used¹⁸⁻²⁰. 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 predicated by Hammond postulate²¹ for a SET mechanism, a better correlation should have been observed with σ^+ values. Thus, 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^{13, 22}. In the study of electronic effect of oxomanganese(V) complexes the observed positive ρ value of 0.38 is in favor of electrophilic attack of oxidant on the sulfide sulfur^{13,23}. The significant increase in the rate of oxidation with increase in the concentration of trichloroacetic acid demonstrates the electrophilic nature of the oxidant and the protonated species is more electrophilic, thereby favouring the reaction^{13,23}. Also, the rate enhancement with increase in the polarity of the medium indicates the formation of a charge-separated transition state which is in favor of the S_N2 mechanism for the oxo(salen)manganese(V) oxidation of organic sulfides¹³.

Conclusion

In comparison with the data reported on the oxidation of organic sulfides by various Schiff base complexes, (salen)Mn^{III}/NaIO₄ system shows the high efficiency of oxidation and follows an S_N2 mechanism (scheme 3).



Scheme-3

The proposed mechanism envisages the formation of intermediate I in the rate-limiting electrophilic attack of the oxo complex on the sulfide, which then decomposes to give (salen)Mn^{III} and sulfoxide as the product. The ΔH^\ddagger (47 to 93 kJ mol⁻¹) and ΔS^\ddagger (-72 to -279 JK⁻¹ mol⁻¹) values are in favor of two electron transfer rather than single electron transfer in the rate-limiting step of the reaction^{25,26}.

Although the correlation between ΔH^\ddagger and ΔS^\ddagger is poor ($r = 0.866$), a plot of $\log k_2$ at 20°C vs. $\log k_2$ at 40°C is linear (figure 6; $r = 0.994$, slope = 0.766, $s = 0.09$) indicating that all the sulfides are oxidized by a similar mechanism²⁷⁻²⁹. The ΔG^\ddagger values were almost constant for all the investigated substituted sulfides, which confirmed the operation of a common mechanism²⁷⁻²⁹.

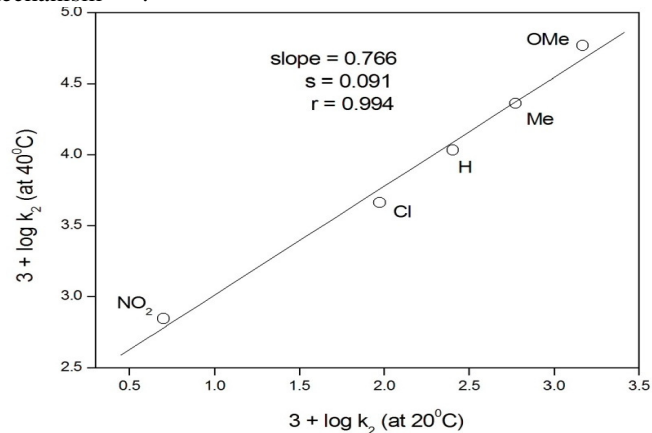


Figure-6
Plot of $\log k_2$ at 20°C vs. $\log k_2$ at 40°C

Acknowledgments

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