# Mechanism of (Salen)manganese(III)-Catalyzed Oxidation of Aryl Phenyl Sulfides with Sodium Hypochlorite

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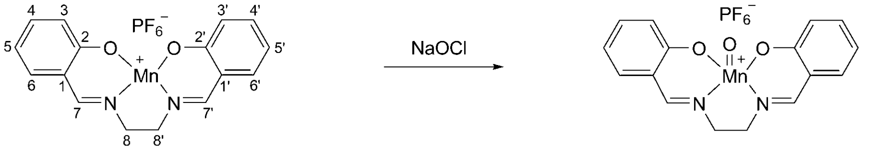
The oxidation of 4-substituted phenyl phenyl sulfides was carried out with several oxo(salen)manganese(V) complexes in MeCN/$H_2O$ 9:1. The kinetic data show that the reaction is first-order each in the oxidant and sulfide. Electron-attracting substituents in the sulfides and electron-releasing substituents 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 $\rho$ value ($\rho = -2.16$) indicating an electron-deficient transition state. The log $k_2$ values observed in the oxidation of each 4-substituted phenyl phenyl sulfide by substituted oxo(salen)manganese(V) complexes also correlate with *Hammett* $\sigma$ constants, giving a positive $\rho$ value. The substituent-, acid-, and solvent-effect studies indicate direct O-atom transfer from the oxidant to the substrate in the rate-determining step.

**Introduction.** – To mimic active intermediates in enzyme-catalyzed oxidation reactions, porphyrinato- and (salen)manganese, -chromium, -ruthenium, and -iron complexes (salen = *N*,*N′*-bis(salicylidene)ethylenediaminato) have been used as model compounds and have been shown to be capable of catalyzing O-atom transfer from monooxygen sources such as PhIO, $H_2O_2$, peracids, NaOCl, $NaIO_4$, *etc.*, to saturated and unsaturated hydrocarbons and other organic substrates [1–14]. Organic sulfides seem to be better substrates than olefins because of the efficient reactivities and of the absence of other undesired reactions [9][12]. Apart from porphyrins, the most important synthetic ligand systems, especially in the context of catalysis for oxidation of organic compounds, are salens [15]. O-Atom transfer from the oxidant to organic sulfides proceeds generally by two different mechanisms. In the oxidation of organic sulfides catalyzed by $Cr^{VI}$ [16], $Ce^{IV}$ [17], tris(2,2′-bipyridyl)iron(III) complexes [18], oxoruthenium(IV) complexes [19], and [$Mn^{III}$(salen)] complexes catalyzed PhIO [20][21], a single-electron-transfer (SET) mechanism has been proposed. On the other hand, the oxidation of sulfides by molybdenum peroxypolyoxo anions [22], pyridinium halochromate [23], permanganate [24], bis(2,2′-bipyridyl)copper(II) permanganate [25], picolinic acid-catalyzed chromium(VI) [26], oxo(salen)chromium(V) [27], and oxo(salen)iron [28] follow an $S_N2$ mechanism. However, a dual mechanism has been proposed in some oxidation reactions [29].

With the aim of establishing the optimum conditions for the synthesis of sulfoxides and sulfones and the mechanism of oxometal ion oxidation of organic sufides, we have studied extensively the kinetics and mechanism of oxo(salen)metal ion oxidation of organic sulfur compounds [20][21][27][30–33]. Recently, we have reported the results on the [$Mn^{III}$(salen)]-catalyzed NaOCl oxidation of aryl methyl sulfides [34][35] and sulfoxides [36]. A diphenyl sulfide may behave differently or similar to that of aryl methyl sulfides. Different mechanisms have been proposed for these two sulfide types in the oxidation studies with peroxo anions [37] and sodium borate [38]. But both the substrates follow a similar mechanism in the *N*-chlorosuccinimide [39], picolinic acid-catalyzed chromium(VI) [26], and [$Mn^{III}$(salen)]-catalyzed PhIO [21] and $H_2O_2$ [31] oxidation reactions. In this article, we report the results of oxidation of 4-substituted phenyl phenyl sulfides with oxo(salen)manganese(V) complexes **2a** – **2f** generated *in situ* from the corresponding [$Mn^{III}$(salen)]($PF_6$) complexes and NaOCl as represented in *Scheme 1*[1]).

*Scheme 1*[1])



**1a** unsubstituted
**1b** 5,5'-$(MeO)_2$
**1c** 5,5'-$Cl_2$
**1d** 5,5'-$(NO_2)_2$
**1e** 7,7'-$Me_2$
**1f** 7,7'-$Ph_2$

**2a** unsubstituted
**2b** 5,5'-$(MeO)_2$
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**2e** 7,7'-$Me_2$
**2f** 7,7'-$Ph_2$

**Results.** – *Oxidative Conversion of (Salen)manganese(III) to Oxo(salen)manganese(V) Species.* The electronic spectra of clear brown solutions of [$Mn^{III}$(salen)] complexes in $MeCN/H_2O$ are characterized by absorption bands with $\lambda_{max}$ *ca.* 350 nm tailing to beyond 400 nm. When a clear brown solution of [$Mn^{III}$(salen)] in $MeCN/H_2O$ was treated with equimolar quantities of sodium hypochlorite, it immediately turns dark brown, indicating the formation of oxomanganese(V) species ($\lambda_{max}$ *ca.* 530 nm) [20][21][33–36]. On standing, the dark brown solution faded to the original light brown one within 2–3 h. When the same experiment was carried out in the presence of diphenyl sulfide (DPS), the dark brown color was discharged to the original light brown one within 20–30 min, and diphenyl sulfoxide was isolated in 68% yield (*Scheme 2*). The absorption spectrum of the final solution coincided with that of the original [$Mn^{III}$(salen)] complex. As the isolation of pure oxo(salen)manganese(V) complexes is difficult [20][21][33–36], they were generated *in situ* for the studies reported here.

*Scheme 2*

$$\mathrm{PhSPh} \xrightarrow[\mathrm{NaOCl}]{[\mathrm{Mn^{III}(salen)}]^+} \mathrm{PhSOPh}$$

*Kinetics of O-Atom Transfer from Oxo(salen)manganese(V) to Sulfides.* The rates of the oxidation of sulfides were measured spectrophotometrically in $MeCN/H_2O$ 9 : 1

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[1]) Arbitrary atom numbering (see *Scheme 1*); the systematic name of salen is {2,2'-[ethane-1,2-diylbis(nitrilomethylidene)]bis[phenolato]}(2 –).

at 20° by following the decay of the oxo(salen)manganese(V) complexes at 680 nm. The rate constants for the oxidation of DPS by **2a**–**2f** are listed in *Table 1*. At constant initial concentration of DPS, constant values of $k_1$ were obtained upon varying the initial concentration of **2a** (*Table 1*); this, coupled with the observation of linear log $(A_t - A_\infty)$ *vs.* time plots ($r > 0.995$), ensures that the order in **2a** is one. The unit slope

Table 1. *Rate Constants for the Oxidation of DPS by* **2a**–**2f** *in MeCN/H$_2$O 9 : 1 at 20°*[a])

| $10^2 \cdot [\mathrm{DPS}]_0$ [M] | $10^3 \cdot [\mathbf{2}]_0$ [M] | $10^4 \cdot k_{1(\mathrm{obs})}$[b]) $[\mathrm{s}^{-1}]$ | $10^4 \cdot k_{1(\mathrm{dec})}$[c]) $[\mathrm{s}^{-1}]$ | $10^4 \cdot k_1$[d]) $[\mathrm{s}^{-1}]$ | $10^3 \cdot k_2$[e]) $[\mathrm{M}^{-1}\,\mathrm{s}^{-1}]$ |
|---|---|---|---|---|---|
| | **2a** | | | | |
| 10.0 | 1.00 | 8.00 ± 0.10 | 5.44 ± 0.09 | 2.56 ± 0.01 | 2.56 ± 0.01 |
| 10.0 | 1.60 | 8.34 ± 0.26 | 5.72 ± 0.16 | 2.62 ± 0.10 | 2.62 ± 0.10 |
| 10.0 | 2.00 | 7.91 ± 0.12 | 5.24 ± 0.09 | 2.67 ± 0.03 | 2.67 ± 0.03 |
| 10.0 | 2.60 | 8.01 ± 0.06 | 5.52 ± 0.03 | 2.49 ± 0.03 | 2.49 ± 0.03 |
| 10.0 | 3.00 | 8.39 ± 0.20 | 5.79 ± 0.16 | 2.60 ± 0.04 | 2.60 ± 0.04 |
| 10.0 | 3.60 | 8.60 ± 0.25 | 5.99 ± 0.05 | 2.61 ± 0.20 | 2.61 ± 0.20 |
| 20.0 | 2.60 | 10.60 ± 0.1 | 5.52 ± 0.03 | 5.08 ± 0.07 | 2.54 ± 0.04 |
| 40.0 | 2.60 | 15.90 ± 0.4 | 5.52 ± 0.03 | 10.40 ± 0.4 | 2.60 ± 0.10 |
| 50.0 | 2.60 | 18.80 ± 0.4 | 5.52 ± 0.03 | 13.30 ± 0.4 | 2.66 ± 0.08 |
| 100.0 | 2.60 | 29.50 ± 0.8 | 5.52 ± 0.03 | 24.00 ± 0.8 | 2.40 ± 0.08 |
| | **2b** | | | | |
| 10.0 | 2.60 | 6.56 ± 0.19 | 4.68 ± 0.04 | 1.88 ± 0.15 | 1.88 ± 0.15 |
| 20.0 | 2.60 | 8.57 ± 0.18 | 4.68 ± 0.04 | 3.89 ± 0.14 | 1.95 ± 0.07 |
| 50.0 | 2.60 | 14.20 ± 0.6 | 4.68 ± 0.04 | 9.52 ± 0.56 | 1.90 ± 0.11 |
| 100.0 | 2.60 | 23.90 ± 0.6 | 4.68 ± 0.04 | 19.2 ± 0.6 | 1.92 ± 0.06 |
| | **2c** | | | | |
| 5.0 | 2.60 | 7.31 ± 0.30 | 5.59 ± 0.07 | 1.72 ± 0.23 | 3.44 ± 0.46 |
| 10.0 | 2.60 | 9.27 ± 0.24 | 5.59 ± 0.07 | 3.68 ± 0.17 | 3.68 ± 0.17 |
| 20.0 | 2.60 | 12.90 ± 0.4 | 5.59 ± 0.07 | 7.31 ± 0.33 | 3.66 ± 0.17 |
| 50.0 | 2.60 | 23.20 ± 0.7 | 5.59 ± 0.07 | 17.60 ± 0.6 | 3.52 ± 0.12 |
| | **2d** | | | | |
| 2.5 | 2.60 | 8.26 ± 0.24 | 5.97 ± 0.04 | 2.29 ± 0.20 | 9.16 ± 0.80 |
| 10.0 | 2.60 | 14.40 ± 0.3 | 5.97 ± 0.04 | 8.43 ± 0.26 | 8.43 ± 0.26 |
| 20.0 | 2.60 | 23.90 ± 0.7 | 5.97 ± 0.04 | 17.90 ± 0.7 | 8.95 ± 0.35 |
| 25.0 | 2.60 | 27.20 ± 0.9 | 5.97 ± 0.04 | 21.20 ± 0.9 | 8.48 ± 0.36 |
| | **2e** | | | | |
| 10.0 | 2.60 | 8.03 ± 0.13 | 5.56 ± 0.06 | 2.47 ± 0.07 | 2.47 ± 0.07 |
| 20.0 | 2.60 | 10.10 ± 0.4 | 5.56 ± 0.06 | 4.54 ± 0.34 | 2.27 ± 0.17 |
| 50.0 | 2.60 | 17.20 ± 0.7 | 5.56 ± 0.06 | 11.60 ± 0.6 | 2.32 ± 0.12 |
| 100.0 | 2.60 | 28.60 ± 0.9 | 5.56 ± 0.06 | 23.00 ± 0.8 | 2.30 ± 0.08 |
| | **2f** | | | | |
| 10.0 | 2.60 | 7.30 ± 0.23 | 5.29 ± 0.07 | 2.01 ± 0.16 | 2.01 ± 0.16 |
| 20.0 | 2.60 | 9.44 ± 0.18 | 5.29 ± 0.07 | 4.15 ± 0.11 | 2.08 ± 0.06 |
| 50.0 | 2.60 | 16.00 ± 0.5 | 5.29 ± 0.07 | 10.70 ± 0.4 | 2.14 ± 0.08 |
| 100.0 | 2.60 | 25.80 ± 0.9 | 5.29 ± 0.07 | 20.50 ± 0.8 | 2.05 ± 0.08 |

[a]) As determined by a spectrophotometric technique following the disappearance of oxomanganese(V) at 680 nm; the error quoted in the $k$ 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 $k_1 = k_{1(\mathrm{obs})} - k_{1(\mathrm{dec})}$. [e]) Individual $k_2$ values estimated as $k_1/[\mathrm{DPS}]_0$.

observed from log–log plots of $k_1$ and $[\mathrm{DPS}]_0$ and the linear plots of $k_1$ *vs.* $[\mathrm{DPS}]_0$ which pass through the origin (*Fig. 1*; $r > 0.997$) establish that the reaction is first-order in sulfide. Hence, the reaction is overall second-order, first-order in each reactant. Similar kinetics were observed for the oxidation of 4-substituted phenyl phenyl sulfides with oxo(salen)manganese(V) complexes **2a**–**2f** (*Fig. 1*). Therefore, the rate law can be given by *Eqn. 1.*

$$\frac{-\mathrm{d}[2]}{\mathrm{d}t} = k_2[\mathbf{2}]\ [\mathrm{sulfide}] \tag{1}$$

The effect of the donor ligand on the reaction rate was determined by measuring $k_1$ at various concentrations of added pyridine *N*-oxide (PyO). The rate data in *Table 2* indicate that PyO has no appreciable effect on the reaction rate. This demonstrates that PyO is not binding with the oxo(salen)manganese(V) complex and has no catalytic effect during the oxidation process. Similar results have been obtained in the epoxidation of olefins [7] and in the oxidation of aryl methyl sulfides [20][34], aryl phenyl sulfides [21], sulfoxides [33][36], and arylthioacetic acids [40] by oxo(salen)-manganese(V) complexes. The observed result is consistent with the observation that the porphyrinatomanganese complexes lack affinity for the sixth axial ligand [41]. To understand the effect of acid and solvent composition on the kinetics of this reaction,

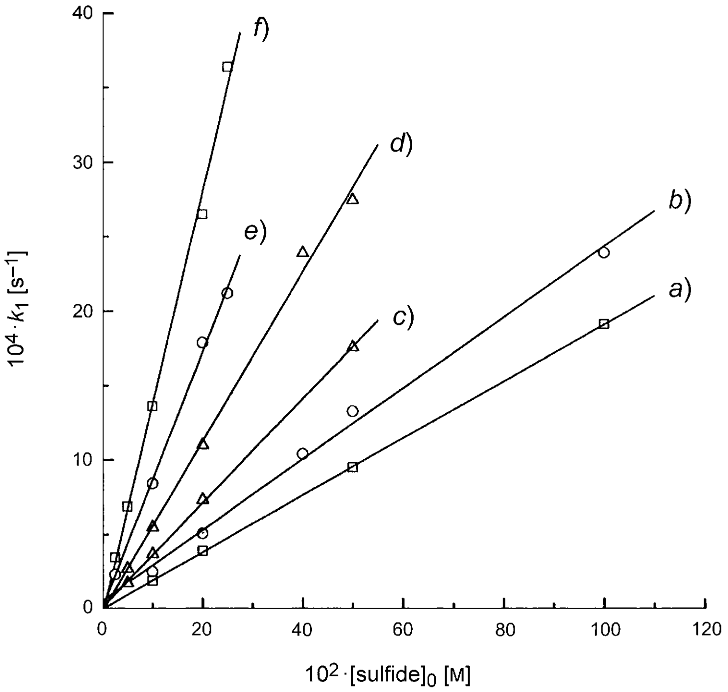


Fig. 1. *Plots of* $k_1$ vs. *[sulfide]$_0$ for the oxidation of* a) *DPS with* **2b**, b) *DPS with* **2a**, c) *DPS with* **2c**, d) *4-MeC$_6$H$_4$SPh with* **2a**, e) *DPS with* **2d**, *and* f) *4-MeOC$_6$H$_4$SPh with* **2a**

Table 2. *Effect of Pyridine* N-*Oxide on the Rate of Oxidation of DPS by* **2a** *in MeCN/H$_2$O 9 : 1 at 20°*[a])

| $10^2 \cdot$ [DPS]$_0$ [M] | $10^3 \cdot$ [**2**]$_0$ [M] | $10^2 \cdot$ [PyO] [s$^{-1}$] | $10^4 \cdot k_{1(\text{obs})}$[b]) [s$^{-1}$] | $10^4 \cdot k_{1(\text{dec})}$[c]) [s$^{-1}$] | $10^4 \cdot k_1$[d]) [M$^{-1}$ s$^{-1}$] | $10^3 \cdot k_2$[e]) [M$^{-1}$ s$^{-1}$] |
|---|---|---|---|---|---|---|
| 10.0 | 2.60 | 0.0 | 8.04 ± 0.06 | 5.52 ± 0.03 | 2.52 ± 0.03 | 2.52 ± 0.03 |
| 10.0 | 2.60 | 2.5 | 8.28 ± 0.19 | 5.44 ± 0.07 | 2.84 ± 0.12 | 2.84 ± 0.12 |
| 10.0 | 2.60 | 5.0 | 8.11 ± 0.19 | 5.39 ± 0.04 | 2.72 ± 0.14 | 2.72 ± 0.14 |
| 10.0 | 2.60 | 10.0 | 7.90 ± 0.28 | 5.02 ± 0.10 | 2.88 ± 0.18 | 2.88 ± 0.18 |
| 10.0 | 2.60 | 20.0 | 8.76 ± 0.22 | 5.89 ± 8.08 | 2.87 ± 0.14 | 2.87 ± 0.14 |
| 10.0 | 2.60 | 25.0 | 8.50 ± 0.29 | 5.60 ± 0.11 | 2.90 ± 0.18 | 2.90 ± 0.18 |

[a]) As determined by a spectrophotometric technique following the disappearance of oxomanganese(V) at 680 nm; the error quoted in the $k$ 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 $k_1 = k_{1(\text{obs})} - k_{1(\text{dec})}$. [e]) Individual $k_2$ values estimated as $k_1$/[DPS]$_0$.

Table 3. *Effect of Adding Acid or Changing the Solvent Composition on the Rate of Oxidation of DPS by* **2a** *at 20°*[a])[b])

| $10^2$ [acid][c]) [M] | $10^4$ [$k_1$][d]) [s$^{-1}$] | MeCN/H$_2$O | $10^4$ $k_1$[e]) [s$^{-1}$] |
|---|---|---|---|
| 0.0 | 2.49 ± 0.03 | 90 : 10 | 5.08 ± 0.07 |
| 0.5 | 3.52 ± 0.03 | 85 : 15 | 8.55 ± 0.29 |
| 1.0 | 6.00 ± 0.18 | 80 : 20 | 11.30 ± 0.4 |
| 5.0 | 24.80 ± 0.7 | 75 : 25 | 14.90 ± 0.7 |
| 10.0 | 42.10 ± 1.8 | 70 : 30 | 17.40 ± 0.9 |
| 20.0 | 98.30 ± 4.0 | | |

[a]) General condition : [**2a**]$_0$ = 0.0026M. [b]) In the evaluation of rate constants, the self-decomposition of **2a** at different [acid] or solvent composition is taken into account. [c]) CCl$_3$COOH. [d]) [DPS]$_0$ = 0.10M; Solvent MeCN/H$_2$O 9 : 1. [e]) [DPS]$_0$ = 0.20M.

the rates at different concentrations of CCl$_3$COOH and solvent compositions were measured (see *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.

The effect of the substituent present at the 4-position of the substituted phenyl phenyl sulfides on the reaction rate was also studied (see *Table 4*). Electron-attracting substituents at the phenyl ring reduce the rate, while electron-releasing substituents enhance the rate. The log $k_2$ values are better correlated with $\sigma_p$ constants (*Fig. 2*; $r = 0.997$, $\rho = -2.16 \pm 0.09$, $s = 0.075$) than with $\sigma^+/\sigma^-$ constants ($r = 0.987$, $\rho = -1.36 \pm 0.13$, $s = 0.169$). The negative $\rho$ value indicates an accumulation of positive charge at the S-atom, and the magnitude of the $\rho$ value indicates the extent of charge development at the S-atom in the transition state of the rate-limiting step [42]. The effect of altering the electronic nature of the oxidant on the rate of oxidation of the 4-substituted phenyl phenyl sulfides was studied with the 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 reduce the

Table 4. *Second-Order Rate Constants and ρ Values for the Reactions of 4-X–$C_6H_4SPh$ with Oxo(salen)manganese(V) Complexes* **2a**–**2d** *in $MeCN/H_2O$ 9 : 1 at 20°*[a])[b])

| X | $10^3 \cdot k_2$ [$M^{-1}$ $s^{-1}$] | | | | ρ[d]) | (*r*) |
|---|---|---|---|---|---|---|
| | **2b** | **2a** | **2c** | **2d** | | |
| MeO | 11.70 ± 0.6 | 13.30 ± 0.40 | 19.80 ± 0.90 | 29.30 ± 1.1 | 0.200 ± 0.027 | (0.982) |
| Me | 4.36 ± 0.18 | 5.50 ± 0.10 | 7.75 ± 0.35 | 13.90 ± 0.6 | 0.245 ± 0.013 | (0.997) |
| H | 1.95 ± 0.07 | 2.54 ± 0.04 | 3.66 ± 0.17 | 8.95 ± 0.35 | 0.322 ± 0.022 | (0.995) |
| Cl | 0.66 ± 0.08 | 0.92 ± 0.07 | 1.89 ± 0.09 | 3.67 ± 0.13 | 0.362 ± 0.045 | (0.982) |
| $NO_2$[c]) | 0.03 ± 0.01 | 0.06 ± 0.01 | 0.17 ± 0.03 | 0.60 ± 0.07 | 0.629 ± 0.058 | (0.992) |
| ρ[e]) | – 2.38 ± 0.12 | – 2.16 ± 0.09 | – 1.86 ± 0.13 | – 1.55 ± 0.09 | | |
| (*r*) | (0.997) | (0.997) | (0.992) | (0.995) | | |

[a]) The error quoted in $k_2$ is the 95% confidence limit of *Student*'s *t*-test. [b]) General conditions: $[\mathbf{2}]_0 = 0.0026$M; $[\text{sulfide}]_0 = 0.20$M. [c]) $[\text{sulfide}]_0 = 0.50$M. [d]) The ρ values were obtained by correlating log $k_2$ with 2 $\sigma_p$ for the reaction of various oxo(salen)manganese(V) complexes with a given sulfide. [e]) The ρ values were obtained by correlating log $k_2$ with $\sigma_p$ for the reaction of various sulfides with a given oxo(salen)manganese(V) complex.

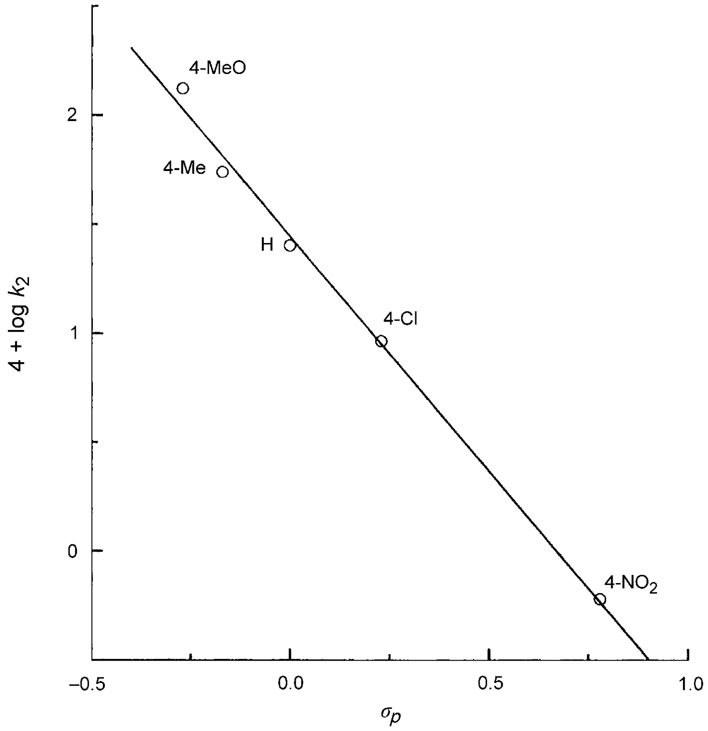


Fig. 2. Hammett *plot for the oxidation of 4-substituted phenyl phenyl sulfides by* **2a**

rate, while electron-attracting substituents enhance it. The *Hammett* correlation of log $k_2$ with 2 $\sigma_p$ is excellent with a ρ value of 0.32 ± 0.02 (*Fig. 3*; $r = 0.995$, $s = 0.035$). The

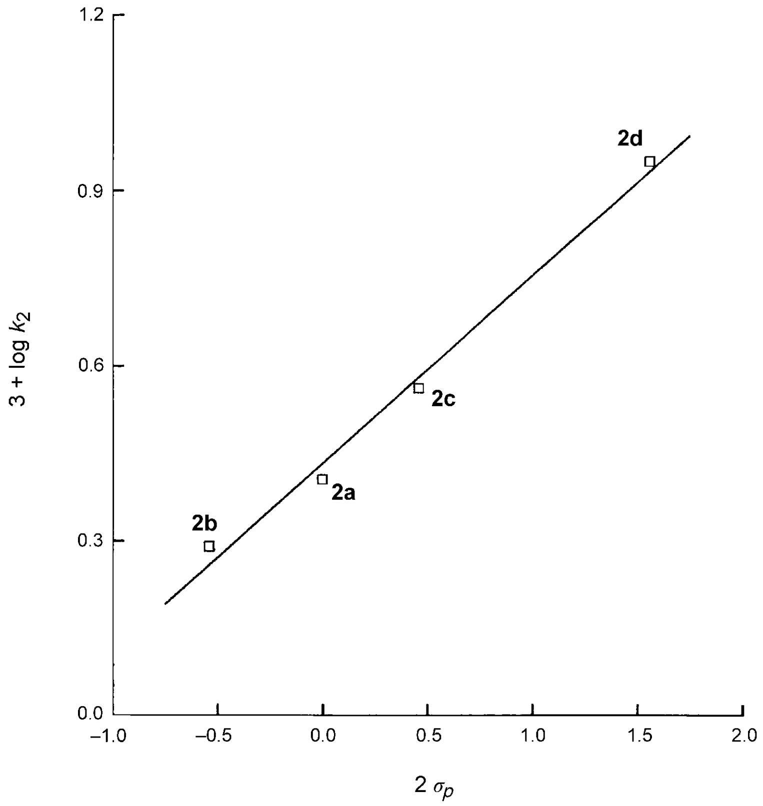


Fig. 3. Hammett *plot for the oxidation of DPS by substituted oxo(salen)manganese(V) complexes*

positive $\rho$ value indicates the build-up of negative charge at the metal center in the transition state of the rate-determining step. 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 as in the case of aryl methyl sulfides [20][34], sulfoxides [33][36], and arylthioacetic acids [40].

The oxo(salen)manganese(V) oxidation of 4-substituted phenyl phenyl sulfides was also carried out at four different temperatures (see *Table 5*). The activation parameters for the oxidation were evaluated from the slope and intercept of the *Eyring* plot of log ($k_2/T$) against $1/T$. The $\Delta H^{\neq}$ (50–70 kJ mol$^{-1}$) and $\Delta S^{\neq}$ (−106 to −84 J K$^{-1}$ mol$^{-1}$) values are in favor of a two-electron transfer rather than a single-electron transfer in the rate-determining step of the reaction [26][27][34][43][44].

**Discussion.** – Mechanistic studies of (salen)metal-catalyzed oxidations are important not only from the stand point of understanding enzymatic oxidations but also for the development of new synthetic methods. Oxo(salen)metal complexes

Table 5. *Second-Order Rate Constants and Activation Parameters for the Oxidation of 4-X–$C_6H_4SPh$ by* **2a** *in $MeCN/H_2O$ 9 : 1 at Four Different Temperatures*[a])

| X | $10^3 \cdot k_2$ [M$^{-1}$ s$^{-1}$] | | | | $\Delta H^{\neq}$ [kJ mol$^{-1}$] | $-\Delta S^{\neq}$ [J K$^{-1}$ mol$^{-1}$] |
|---|---|---|---|---|---|---|
| | 293 K | 298 K | 303 K | 313 K | | |
| MeO[b]) | 13.60 ± 0.50 | 20.70 ± 1.0 | 28.90 ± 1.4 | 56.50 ± 2.0 | 51.3 | 106 |
| Me | 5.50 ± 0.10 | 8.90 ± 0.35 | 12.00 ± 0.7 | 22.60 ± 1.1 | 50.3 | 116 |
| H | 2.54 ± 0.04 | 3.51 ± 0.22 | 5.25 ± 0.15 | 10.20 ± 0.4 | 51.0 | 120 |
| Cl | 0.92 ± 0.07 | 1.41 ± 0.12 | 1.98 ± 0.11 | 4.00 ± 0.35 | 52.3 | 122 |
| $NO_2$[c]) | 0.06 ± 0.01 | 0.11 ± 0.00 | 0.17 ± 0.04 | 0.42 ± 0.08 | 70.6 | 84.2 |

[a]) General conditions: [**2a**]$_0$ = 0.0026M; [sulfide]$_0$ = 0.20M, unless otherwise noted. [b]) [sulfide]$_0$ = 0.10M. [c]) [sulfide]$_0$ = 0.50M.

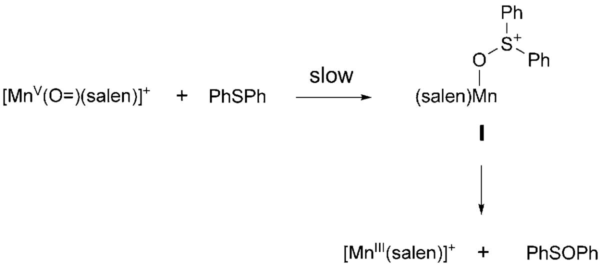
[20][21][27][28][33–36][40] have drawn increased attention as viable oxidation catalysts for O-atom transfer to biochemically important organic sulfur compounds. These reactions could be the result of a direct O-atom transfer from oxo(salen)metal complexes to the S-atom of the organic sulfur compounds [27][28][33–36], or alternatively the reactions could be initiated by a single-electron transfer from the S-atom to the metal followed by recombination of the sulfur radical cation and the reduced oxo(salen)metal complexes to give an oxygen-rebound mechanism [20][21][45][46].

*Mechanism of Oxo(salen)manganese(V) Oxidation of 4-Substituted Phenyl Phenyl Sulfides.* In the absence of other oxygen sources, as in the present study, there is no doubt that the O-atom incorporated into the substrate is derived from the oxomanganese(V) complex ion. The observation of overall second-order kinetics, first-order each in oxo complex and sulfide, indicates that the reaction follows simple kinetics without involving any complex mechanism. The results obtained from the studies on the influence of changes in the electronic nature of the substrate and oxidant throw more light on the mechanism of O-atom transfer. The observed negative reaction constant ($\rho = -2.16 \pm 0.09$) points to an electrophilic attack at the S-atom by oxidant. Also the observed better correlation of log $k_2$ with $\sigma_p$ than with $\sigma^+/\sigma^-$ may be taken as a clue for the operation of an $S_N2$ mechanism. Furthermore, the substituted oxo(salen)-manganese(V) complexes **2a**–**2d** display an excellent *Hammett* correlation of log $k_2$ with 2 $\sigma_p$ ($\rho = 0.32 \pm 0.02$) in favor of an electrophilic attack of the oxidant at the sulfide S-atom [5][6]. The observed acid and solvent effects (*Table 3*) are very similar to those observed in aryl methyl sulfide oxidations [34][35] where an $S_N2$ mechanism operates.

As all these results are similar to those obtained for the oxidation of aryl methyl sulfides, the aryl methyl and 4-substituted phenyl phenyl sulfides are likely to be oxidized by an $S_N2$ mechanism (*Scheme 3*) [21][26][39]. 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 [Mn$^{III}$(salen)] and sulfoxide as products.

The plot of the log $k_2$ values of substituted phenyl methyl sulfides at 20° is linear, like that of substituted phenyl phenyl sulfides, with a unit slope (slope = 1.17 ± 0.04, $r$ = 0.998, $s$ = 0.064); this also confirms that 4-substituted phenyl phenyl sulfides and aryl

*Scheme 3*



methyl sulfides follow the same mechanism in the oxo(salen)manganese(V) oxidation [21][26][39]. Although the correlation between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ is not satisfactory ($r=$ 0.905) in the present reaction, a plot of log $k_2$ at 20° *vs.* log $k_2$ at 40° (*Exner*'s plot) is linear ($r=0.999$, slope $=0.90\pm0.03$, $s=0.051$) indicating that all the 4-substituted phenyl phenyl sulfides are oxidized by a similar mechanism [26][39]. The excellent correlation obtained in *Exner*'s plots, as in the case of aryl methyl sulfides ($r=0.997$), lead to the conclusion that the mechanism of the reaction of oxo(salen)manganese(V) with aryl methyl sulfides and 4-substituted phenyl phenyl sulfides is one and the same.

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## Experimental Part

*Materials.* Diphenyl sulfide (DPS), 4-methoxy, 4-methyl- and 4-chlorophenyl phenyl sulfides were prepared by *Mauthner*'s method [47] from the corresponding thiophenol and iodobenzene; 4-nitrophenyl phenyl sulfide was obtained from 1-chloro-4-nitrobenzene and thiophenol [48]. The sulfides were purified by distillation under reduced pressure or recrystallization from suitable solvents, and purity was checked by usual methods. NaOCl (*S.D. Fine Chem. Ltd.*) was estimated by iodometric method. MeCN (G. R. *E. Merck*) was purified by refluxing with $P_2O_5$ for 5 h in an all-glass apparatus and then distilled. Double dist. $H_2O$ was used throughout, the second distillation being from permanganate.

The *{{2,2'-{ethane-1,2-diylbis[(nitrilo-κ*N*)methylidyne]}bis[phenolato-κ*O*)}(2−)}manganese(1+) hexafluorophosphates* ([Mn$^{III}$(salen)](PF$_6$)) **1a**–**1f** were synthesized according to a known procedure [7][20][33]. The IR and UV/VIS spectral studies of all the complexes were found to be identical with reported data [7]. The *{{2,2'-{ethane-1,2-diylbis[(nitrilo-κ*N*)methylidyne]}bis[phenolato-κ*O*)}(2−)}oxomanganese(1+) hexafluorophosphates* [Mn$^V$(O=)(salen)](PF$_6$)) **2a**–**2f** were obtained by mixing equimolar quantities of complex **1** and NaOCl. Because the oxomanganese(V) complexes **2** undergoes auto-decomposition, the solns. were prepared freshly for each kinetic run.

*Kinetic Measurements.* The kinetic studies were carried out in MeCN/$H_2O$ 9 : 1 at 20 ± 0.1° under pseudo-first-order conditions ([sulfide] > [oxo complex]) with a *Perkin-Elmer* UV/VIS spectrophotometer (*Lambda 3B*), fitted with thermostated cell compartments. Reaction mixtures for kinetic runs were prepared by quickly mixing the solns. of the oxo complex **2** 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 disappearance of the oxomanganese(V) complex **2** at 680 nm [7][20][33].

The rate constants were computed from the linear least-square plots of log ($A_t - A_\infty$) *vs.* time, where $A_t$ is the absorbance at time $t$, and $A_\infty$ is the experimentally determined infinity value. The values of $k_1$ were obtained from $k_1 = k_{1(\mathrm{obs})} - k_{1(\mathrm{dec})}$, where $k_{1(\mathrm{dec})}$ represents the first-order rate constants for the auto-decomposition of oxo complex **2**, and $k_{1(\mathrm{obs})}$ represents the pseudo-first-order rate constants for the decay of oxo complex **2** in the presence of sulfides. The second-order rate constants, $k_2$, were obtained by the relation $k_2 = k_1/[\mathrm{sulfide}]$.

*Stoichiometry and Product Analysis.* The reaction studied under the experimental conditions ($[\mathbf{2a}] = 0.0026\,\mathrm{M}$; $[\mathrm{PhSPh}] = 0.20\,\mathrm{M}$) gave the sulfoxide PhSOPh in *ca.* 68% yield, and the $[\mathrm{Mg^{III}(salen)}]$ complex in *ca.* 95% yield, with a negligible amount of sulfone. Accordingly, the stoichiometry of the reaction can be represented by *Scheme 4*.

*Scheme 4*

$$[\mathrm{Mn^{V}(O{=})(salen)}]^{+} + \mathrm{PhSPh} \longrightarrow [\mathrm{Mn^{III}(salen)}]^{+} + \mathrm{PhSOPh}$$

The reaction mixture from an actual kinetic run was concentrated to remove the solvent, the residue then extracted with $CHCl_3$, and the extract dried ($Na_2SO_4$) and concentrated. GC Analysis of the residue (*GC17A-Schimadzu* gas chromatograph) indicated the formation of sulfoxide as the only product under the present experimental conditions. The yield of sulfoxide (65–75%) depended on the sulfide and oxomanganese(V) complex employed.

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