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# Oxidation of Aryl Methyl Sulfoxides by Oxo(salen)manganese(V) Complexes and the Reactivity−Selectivity Principle[†]

Arunachalam Chellamani,[*,‡] Periasamy Kulanthaipandi,[‡] and Seenivasan Rajagopal[*,§]

*Department of Chemistry, Manonmaniam Sundaranar University, Tirunelveli 627 012, and School of Chemistry, Madurai Kamaraj University, Madurai 625 021, India*

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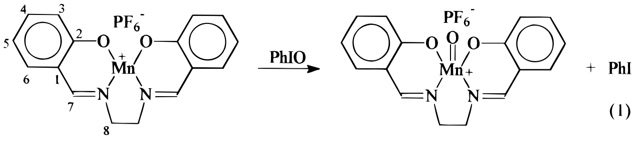
The oxidation of various para-substituted phenyl methyl sulfoxides with several substituted oxo(salen)manganese(V) complexes follows an overall second-order kinetics that is first-order in sulfoxide and in oxo(salen)manganese(V) complex. Electron-releasing substituents in sulfoxides and electron-withdrawing substituents in oxo(salen)manganese(V) complexes enhance the rate of oxidation. The less nucleophilic sulfoxides are more sensitive to substituent effect ($\rho = -2.44$) compared to the corresponding sulfides ($\rho = -1.86$). These results are interpreted with a common mechanism involving the electrophilic attack of the oxidant on the sulfur center of the substrate. Correlation analyses show the presence of an inverse relationship between reactivity and selectivity in the reactions of various sulfoxides with a given oxo(salen)manganese(V) complex and vice versa. Mathematical treatment of the results leads to the conclusion that this redox system falls under strong reactivity−selectivity principle.

## Introduction

Organic sulfides and sulfoxides are interesting substrates that have many similarities but some differences in their reactions with oxidants. Whereas organic sulfides behave always as strong nucleophiles, sulfoxides act as biphilic substrates if strong and rather unselective oxidants are used. It is well known that organic sulfoxides are less powerful nucleophiles compared to the corresponding organic sulfides and thus less reactive towards electrophilic reagents. With many oxidants, it has been established that the ratio of reactivity, $k_s/k_{so}$, is very large and the nucleophilic reactivity of thioethers is more affected by structural effects than that of sulfoxides.[1−5] Comparison of reaction constant ($\rho$) values points out that the values for thioether oxidation are consistently larger than those of sulfoxides.[6−10] The low $\rho$ values (selectivity) in conjunction with the low reactivity of sulfoxides compared to sulfides leads us to infer that the selectivity decreases with the decreasing reactivity of sulfoxides compared to sulfides.[6−10]

Recently, we have reported the mechanism of the oxidation of organic sulfides by oxo(salen)manganese(V) complexes and also the successful application of the reactivity−selectivity principle (RSP) to this oxidation.[11] To understand whether the organic sulfoxides follow a mechanism similar to that of sulfides towards the oxidant oxo(salen)manganese(V) and the relevance of RSP in this redox system, we have studied spectrophotometrically the kinetics of oxidation of several aryl methyl sulfoxides with the six oxo(salen)manganese(V) complexes **2a-f** generated in situ from the corresponding $[\mathrm{Mn^{III}(salen)}]^+\mathrm{PF_6}^-$ complexes and PhIO as represented in eq 1; the results of these studies are analyzed in this article.



**1** **2** (1)

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

Although we have assumed the active Mn species to be the reactive (salen)Mn(V) oxo intermediate ((salen)-

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[†] Dedicated to Professor C. Srinivasan on his sixtieth year.

[‡] Manonmaniam Sundaranar University.

[§] Madurai Kamaraj University.

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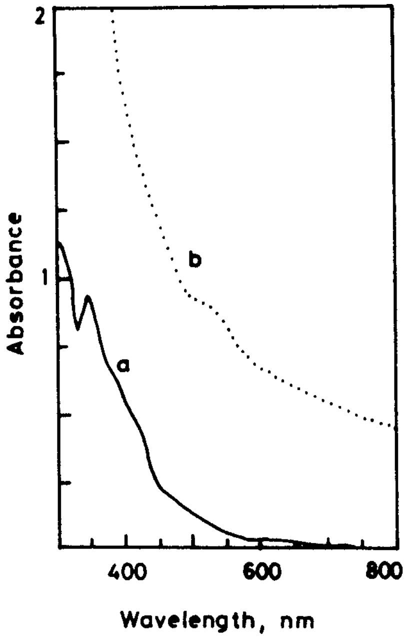

**Figure 1.** (a) Absorption spectrum of **1a** (0.0018 M) in acetonitrile taken in a 1 cm cuvette. (b) Absorption spectrum of oxo(salen)manganese(V) complex **2a** (0.0018 M).

$Mn^V{=}O$) by comparing the present spectral observations with the previous reports,[11] we could not isolate this active species. It is pertinent to point out that to date no (salen)Mn(V) oxo species have yielded to structural characterization, although Groves et al. and others have characterized oxomanganese(V) porphyrin complexes in recent years.[12] We have chosen the salen ligand because it is similar to porphyrin and the electronic and steric nature of the metal complex can be tuned by introducing electron-withdrawing and electron-releasing substituents and bulky groups in the ligand.

## Results and Discussion

**Oxidative Conversion of Manganese(III) to Oxomanganese(V) Species.** The stirring of clear brown solutions 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 1. The formation of oxomanganese(V) species is invariably associated with the following two changes: (i) the light brown color darkens, and (ii) the characteristic peak of (salen)$Mn^{III}$ at $\lambda_{max} \approx 350$ nm disappears and a new absorption band at $\lambda_{max} \approx 530$ nm appears (Figure 1). The dark brown solution, on standing, faded to the original light brown within 2−3 h. When methyl phenyl sulfoxide (MPSO) was added to the dark brown solution, the fading occurred in less than 40−50 min and methyl phenyl sulfone was isolated in 79% yield (eq 2). The absorption spectrum of the final solution coincided with that of the original (salen)$Mn^{III}$ complex.

$$\mathrm{PhSOMe} \xrightarrow[\mathrm{PhIO}]{(\mathrm{salen})\mathrm{Mn}^{\mathrm{III}}} \mathrm{PhSO_2Me} + \mathrm{PhI} \qquad (2)$$

We have attempted to get a stable oxo(salen)$Mn^V$ complex. 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, the isolated solid was found to be impure compared to an in situ generated solution of **2a**, on the basis of their reported spectroscopic characterization. Therefore, the oxomanganese(V) complexes were generated in situ for the studies reported here. It is pertinent to recall that Kochi and co-workers have taken the formation of peaks at 530 and 550 nm as spectral evidence of the oxomanganese(V) complex when the parent salen and 5,5′-$(NO_2)_2$-salen were taken as the ligands.[13]

**Kinetics of Sulfoxide Oxidation with Oxo(salen)-manganese(V).** Reaction rates were measured spectrophotometrically in acetonitrile at 25 °C by following the decay of the oxomanganese(V) species at 680 nm. At a constant initial concentration of sulfoxide, 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 reveals that variation of the initial concentration of sulfoxide at constant [**2a**] resulted in variation of the $k_1$ values. A plot of $k_1$ versus [sulfoxide] yielded a straight line passing through the origin (Figure 2), indicating that the reaction is overall second-order and first-order in each reactant. Similar kinetics were observed for the oxidation of substituted phenyl methyl sulfoxides with oxomanganese(V) complexes **2a-f** (Figure 2). Therefore, the rate law can be depicted as in eq 3.

$$-\mathrm{d}[\mathbf{2}]/\mathrm{d}t = k_2[\mathbf{2}][\mathrm{sulfoxide}] \qquad (3)$$

The effect of substituents at the para position of the phenyl ring of phenyl methyl sulfoxide was studied using several para-substituted phenyl methyl sulfoxides. The second-order rate constants for the reaction of these para-substituted sulfoxides with **2a** are given in Table 2. Electron-releasing substituents in the phenyl ring accelerate the rate, whereas electron-withdrawing substituents produce the opposite effect. The log $k_2$ values show better correlation with $\sigma_p$ (Figure 3; $r = 0.997$; $\rho = -2.44 \pm 0.60$; $s = 0.079$) than with $\sigma^+/\sigma^-$ ($r = 0.984$; $\rho^+ = -1.54 \pm 0.89$; $s = 0.184$). The negative $\rho$ value indicates an accumulation of positive charge at the sulfur center, and the magnitude of the $\rho$ value indicates the extent of charge development on the sulfur atom in the transition state of the rate-determining step.[14]

The electronic effects on the reactivity of oxomanganese(V) complexes can be studied by having the substituents at the 5,5′-positions that are para to the pair of ligating oxygen atoms.[13] The effect of altering the electronic nature of the oxidant on the rate of oxidation of methyl phenyl sulfoxide has been studied using oxo(salen)manganese(V) complexes **2a-d**. The second-order rate constants measured from this study are given in Tables 1 and 2. It is seen that the electron-withdrawing substituents at the 5,5′-positions of the salen ligand enhance the rate, whereas electron-releasing substituents

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**Table 1. Rate Constants for the Oxidation of MPSO by Oxo(salen)manganese(V) Complexes 2a–f in Acetonitrile at 25 °C**[a]

| $10^2$[MPSO], M | $10^3$[**2**], M | $10^4\ k_{1(\mathrm{obs})}$,[b] $\mathrm{s}^{-1}$ | $10^4\ k_{1(\mathrm{dec})}$,[c] $\mathrm{s}^{-1}$ | $10^4\ k_1$,[d] $\mathrm{s}^{-1}$ | $10^3\ k_2$,[e] $\mathrm{M}^{-1}\ \mathrm{s}^{-1}$ |
|---|---|---|---|---|---|
| | | | **2a** | | |
| 20 | 0.83 | 11.4 ± 0.4 | 5.26 ± 0.14 | 6.14 ± 0.26 | 3.07 ± 0.13 |
| 20 | 1.24 | 11.7 ± 0.6 | 5.23 ± 0.25 | 6.47 ± 0.35 | 3.24 ± 0.18 |
| 20 | 1.65 | 11.0 ± 0.2 | 4.72 ± 0.05 | 6.28 ± 0.15 | 3.14 ± 0.08 |
| 20 | 1.80 | 11.2 ± 0.3 | 4.84 ± 0.09 | 6.36 ± 0.21 | 3.18 ± 0.11 |
| 20 | 2.02 | 11.3 ± 0.3 | 5.15 ± 0.17 | 6.15 ± 0.13 | 3.08 ± 0.07 |
| 20 | 3.04 | 11.5 ± 0.5 | 5.02 ± 0.22 | 6.48 ± 0.28 | 3.24 ± 0.14 |
| 10 | 1.8 | 7.96 ± 0.18 | 4.84 ± 0.09 | 3.12 ± 0.09 | 3.12 ± 0.09 |
| 30 | 1.8 | 14.3 ± 0.4 | 4.84 ± 0.09 | 9.46 ± 0.31 | 3.15 ± 0.10 |
| 40 | 1.8 | 17.6 ± 0.7 | 4.84 ± 0.09 | 12.8 ± 0.6 | 3.20 ± 0.15 |
| 70 | 1.8 | 27.5 ± 1.1 | 4.84 ± 0.09 | 22.7 ± 1.0 | 3.24 ± 0.14 |
| 100 | 1.8 | 36.6 ± 1.7 | 4.84 ± 0.09 | 31.8 ± 1.6 | 3.18 ± 0.16 |
| | | | **2b** | | |
| 8 | 1.8 | 5.06 ± 0.06 | 3.91 ± 0.04 | 1.15 ± 0.02 | 1.44 ± 0.03 |
| 20 | 1.8 | 7.15 ± 0.17 | 3.91 ± 0.04 | 3.24 ± 0.13 | 1.62 ± 0.07 |
| 40 | 1.8 | 10.5 ± 0.3 | 3.91 ± 0.04 | 6.59 ± 0.26 | 1.65 ± 0.07 |
| 80 | 1.8 | 16.0 ± 0.4 | 3.91 ± 0.04 | 12.1 ± 0.4 | 1.51 ± 0.05 |
| | | | **2c** | | |
| 4 | 1.8 | 7.14 ± 0.23 | 5.09 ± 0.16 | 2.05 ± 0.07 | 5.13 ± 0.18 |
| 10 | 1.8 | 10.3 ± 0.3 | 5.09 ± 0.16 | 5.21 ± 0.14 | 5.21 ± 0.14 |
| 20 | 1.8 | 15.8 ± 0.7 | 5.09 ± 0.16 | 10.7 ± 0.5 | 5.35 ± 0.25 |
| 40 | 1.8 | 26.4 ± 1.0 | 5.09 ± 0.16 | 21.3 ± 0.8 | 5.33 ± 0.20 |
| | | | **2d** | | |
| 4 | 1.8 | 13.0 ± 0.3 | 5.14 ± 0.21 | 7.84 ± 0.09 | 19.6 ± 0.2 |
| 10 | 1.8 | 26.4 ± 1.0 | 5.14 ± 0.21 | 21.3 ± 0.8 | 21.3 ± 0.8 |
| 20 | 1.8 | 45.1 ± 1.3 | 5.14 ± 0.21 | 40.0 ± 1.1 | 20.0 ± 0.6 |
| 40 | 1.8 | 81.9 ± 4.1 | 5.14 ± 0.21 | 76.8 ± 3.9 | 19.2 ± 1.0 |
| | | | **2e** | | |
| 8 | 1.8 | 6.38 ± 0.18 | 4.52 ± 0.11 | 1.86 ± 0.07 | 2.33 ± 0.09 |
| 20 | 1.8 | 9.34 ± 0.34 | 4.52 ± 0.11 | 4.82 ± 0.23 | 2.41 ± 0.12 |
| 40 | 1.8 | 14.0 ± 0.4 | 4.52 ± 0.11 | 9.48 ± 0.29 | 2.37 ± 0.07 |
| 80 | 1.8 | 22.7 ± 0.9 | 4.52 ± 0.11 | 18.2 ± 0.79 | 2.28 ± 0.10 |
| | | | **2f** | | |
| 8 | 1.8 | 5.61 ± 0.16 | 4.13 ± 0.14 | 1.48 ± 0.02 | 1.85 ± 0.03 |
| 20 | 1.8 | 7.71 ± 0.23 | 4.13 ± 0.14 | 3.58 ± 0.09 | 1.79 ± 0.05 |
| 40 | 1.8 | 11.0 ± 0.5 | 4.13 ± 0.14 | 6.87 ± 0.36 | 1.72 ± 0.09 |
| 80 | 1.8 | 19.1 ± 0.8 | 4.13 ± 0.14 | 15.0 ± 0.7 | 1.88 ± 0.08 |

[a] As determined by a spectrophotometric technique following the disappearance of the oxo complex at 680 nm; the error quoted in $k$ values is the 95% confidence limit of the Student $t$ test. [b] Estimated from pseudo-first-order plots over 20% reaction. [c] Estimated from first-order plots over 50–60% reaction in the absence of sulfoxide. [d] Obtained as $k_1 = k_{1(\mathrm{obs})} - k_{1(\mathrm{dec})}$. [e] Individual $k_2$ values estimated as $k_1$/[sulfoxide].

retard it. Hammett correlation of log $k_2$ versus $\Sigma\sigma_p$ shows an excellent linear relationship with a slope of 0.52 ± 0.04 (Figure 4; $r = 0.999$; $s = 0.013$). The positive $\rho$ value indicates the buildup of negative charge on the metal center in the transition state of the rate-determining step.[14]

In principle, this sizable electronic effect may be ascribed to any of several factors. The substituents may effect changes in the Mn–oxo bond length in the reactive oxo(salen)Mn$^{\mathrm{V}}$ intermediate, thereby altering the nonbonding substrate–ligand interactions. However, such effects on metal–oxo bond length are reported to be small.[15] Further, the observed results are contrary to what one can expect from this hypothesis. Because electron-withdrawing groups should shorten the Mn–oxo bond length, it must lead to a decrease in reactivity rather than an increase as observed experimentally (compare the reactivity of **2a** and **2d** with sulfoxides). Thus, an alternative explanation must be attempted.

The introduction of the electron-donating substituents in the salen ligand of the Mn(III) complex is expected to stabilize the high-valent Mn(V) oxo intermediate, attenuating its reactivity and thus generating a relatively milder oxidant. Similarly, electron-withdrawing substituents are expected to destabilize the Mn(V) oxo intermediate, making it a more reactive oxidant.[16] This aspect can be substantiated from the $E°$ values of the Mn(II)/Mn(III) redox couple. There is an excellent correlation between $E°$ values of the Mn(II)/Mn(III) redox couple and $\Sigma\sigma_p$ of the 5,5′-substituents (Figure 5; $r = 0.999$; slope = 0.24). Thus, the effect of introducing a 5,5′-substituent in the salen ligand on the redox potential of the metal–oxo complex is mainly responsible for the substituent effect on the rate of the oxygenation reaction. The measurement of the redox potential of the couple Mn(IV)/Mn(V) is not attempted because Mn(IV) and Mn(V) are not stable under the electrochemical reaction conditions. The results of the correlation of kinetic and electrochemical data with Hammett $\sigma$ constants point out an interesting contrast between the oxidant and substrate toward the substituent effect. The dramatic difference between the effect of substitution on the substrate versus that on

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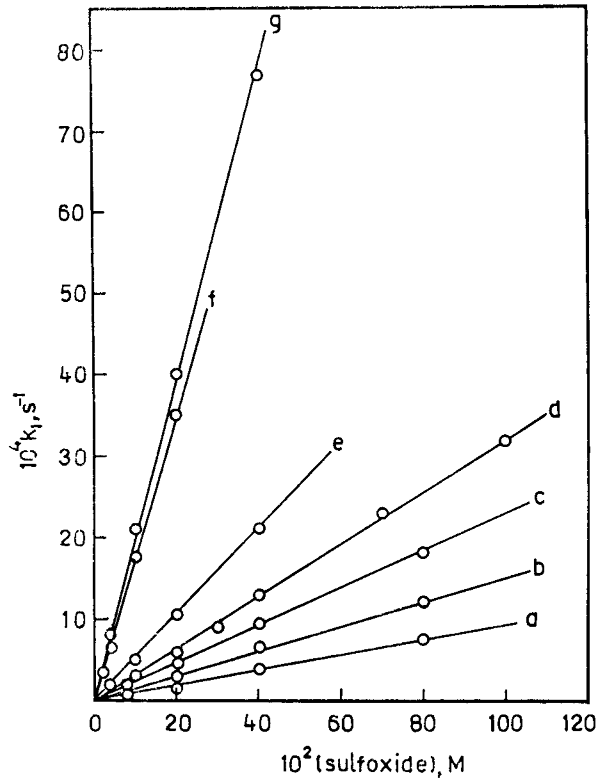

**Figure 2.** Plots of $k_1$ versus [sulfoxide] for the oxidation of (a) *p*-$BrC_6H_4SOMe$ with **2a**, (b) MPSO with **2b**, (c) MPSO with **2e**, (d) MPSO with **2a**, (e) MPSO with **2c**, (f) *p*-$OMeC_6H_4SOMe$ with **2a**, and (g) MPSO with **2d**.

the salen ligand is that the oxidant has an extremely electrophilic oxygen that has very little interaction with the aromatic portion of the salen. This absence of electronic communication could be due to weak M−O $\pi$ bonding or a weak $\pi$ interaction between the salen oxygen and the metal. The slope value (+0.24) obtained in the $E°$ versus $\Sigma\sigma_p$ plot (Figure 5) supports this postulation regarding electronic interaction between ligand and metal and suggests that regardless of oxidation state this interaction is weak.[17] It is interesting to compare the present results with those observed for the oxidation of organic sulfides.[11] The electronic effect is more pronounced with sulfoxide oxidation and the $\rho$ value is uniformly higher with sulfoxides (Tables 2 and 3).

The effect on the reaction rate of introducing substituents at the 7-position of the salen ligand of the oxomanganese(V) complex was studied using **2a**, **2e**, and **2f** for the oxidation of methyl phenyl sulfoxide. The rate data in Table 1 show that the presence of a methyl or phenyl group at the 7-position slightly reduces the rate, as in the case of sulfide oxidation.[11] Thus, the steric effect observed with $\mathrm{Mn^V}$ complexes is little, which is contrary to the substantial steric effect noted in the oxo(salen)-$\mathrm{Cr^V}$ complexes oxidation of alkynes.[18]

**Mechanism of Oxygen Atom Transfer from Oxomanganese(V) to Sulfoxides.** Three types of mechanisms have been proposed so far for the oxidation of sulfoxides. Most of the reactions proceed by a mechanism involving a rate-determining electrophilic attack of the oxidant on the sulfur of the sulfoxide.[19−26] However, a single-electron transfer mechanism from the sulfoxide to the metal ion in the rate-determining step has been postulated in the Cr(VI),[27,28] cytochrome P-450,[29] and tetrahexylammonium tetrakis(diperoxomolybdo)phosphate[30] oxidations of substituted phenyl methyl sulfoxides. On the other hand, in the alkaline peroxobenzoic acid and peroxide oxidation,[31−33] as well as in the fluorenone carbonyl oxide[34] and permanganate ion[35] oxidation of sulfoxides, a nucleophilic attack of the oxidant on the sulfoxide in the rate-determining step has been suggested.

In the present study, the formation of the sulfone in the absence of other oxygen sources (i.e., at inert atmosphere and in non-aqueous solvent) undoubtedly establishes that the oxygen atom incorporated into the sulfone is derived from the oxomanganese(V) ions. The results obtained from the studies on influence of changes in the electronic nature of the substrate and oxidant throw more light on the mechanism of oxygen atom transfer. The observed $\rho$ value of $-2.44 \pm 0.60$ is close to the $\rho$ values found for the oxidation of substituted phenyl methyl sulfoxides by potassium bromate[19] ($\rho = -2.05$) and by chloramine-T[20] ($\rho = -2.02$). These reactions were characterized as proceeding through an electrophilic attack by a halogen ion on the sulfur center of the sulfoxide in the rate-determining step. In the dioxiranes,[22] gem-dialkylperoxonium ion,[23] Cr(VI)-oxalic acid,[24] peroxomonosulfate,[25] and oxo(phosphine)ruthenium(IV) complexes[26] oxidation of substituted phenyl methyl sulfoxides, although low $\rho$ values of −0.76, −0.83, −0.93, −0.40, and −0.42, respectively, have been observed, an $S_N2$ mechanism has been postulated for all these reactions. In the present study, because the observed $\rho$ value is high and log $k_2$ values are better correlated with $\sigma_p$, one may anticipate a $S_N2$ mechanism involving the rate-determining electrophilic attack of the oxidant on the sulfur of the sulfoxide.

A clear picture of the mechanism of this reaction may emerge by comparing the present results with those

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**Table 2. Second-Order Rate Constants and $\rho$ Values for the Reactions of para-Substituted Phenyl Methyl Sulfoxides ($p$-$XC_6H_4SOMe$) with 2a-d in Acetonitrile at 25 °C**[a,b]

| | | oxo(salen)manganese(V) complex, $10^3$ $k_2$, $M^{-1}$ $s^{-1}$ | | | | | |
|---|---|---|---|---|---|---|---|
| no. | X | **2b** | **2a** | **2c** | **2d** | $\rho^d$ | ($r$) |
| 1 | OMe | 13.5 ± 0.7 | 17.6 ± 0.6 | 23.4 ± 1.1 | 41.7 ± 2.0 | 0.235 ± 0.040 | (0.999) |
| 2 | Me | 5.00 ± 0.20 | 7.25 ± 0.15 | 11.2 ± 0.2 | 30.2 ± 1.4 | 0.377 ± 0.074 | (0.998) |
| 3 | H | 1.62 ± 0.07 | 3.18 ± 0.11 | 5.35 ± 0.25 | 20.0 ± 0.6 | 0.518 ± 0.036 | (0.999) |
| 4 | Cl | 0.515 ± 0.020 | 1.21 ± 0.04 | 2.24 ± 0.08 | 7.95 ± 0.25 | 0.559 ± 0.121 | (0.997) |
| 5 | Br | 0.360 ± 0.010 | 0.920 ± 0.050 | 1.95 ± 0.05 | 7.05 ± 0.30 | 0.609 ± 0.152 | (0.994) |
| 6 | $NO_2$[c] | 0.018 ± 0.002 | 0.040 ± 0.004 | 0.078 ± 0.006 | 0.550 ± 0.016 | 0.710 ± 0.068 | (0.999) |
| | $\rho^e$ | −2.67 ± 0.76 | −2.44 ± 0.60 | −2.29 ± 0.70 | −1.80 ± 0.68 | | |
| | ($r$) | (0.996) | (0.997) | (0.995) | (0.993) | | |

[a] The error quoted in $k_2$ is the 95% confidence limit of the Student $t$ test. [b] General conditons: [**2**] = 0.0018 M; [sulfoxide] = 0.20 M. [c] [Sulfoxide] = 0.50 M. [d] The values were obtained by correlating log $k_2$ with $\Sigma\sigma_p$, for the reaction of various oxo(salen)manganese(V) complexes with a given sulfoxide. [e] The values were obtained by correlating log $k_2$ with $\sigma_p$ for the reaction of various sulfoxides with a given oxo(salen)manganese(V) complex.

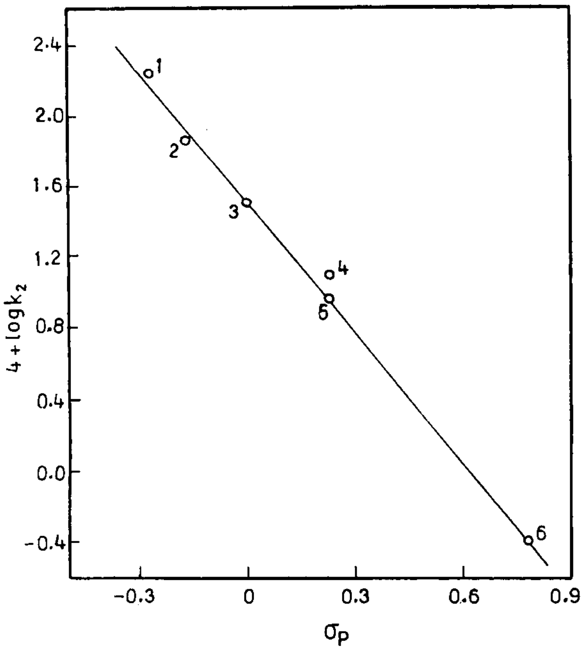


**Figure 3.** Hammett plot for the oxidation of aryl methyl sulfoxides by **2a**. The points are referred to by the same numbers as in Table 2.

observed for the oxo(salen)Mn$^V$ complexes oxidation of organic sulfides[11] (Table 3). It is surprising that the reactivity of organic sulfides and sulfoxides towards these Mn(V) complexes is comparable and the $\rho$ values are always higher with sulfoxides (Tables 2 and 3). As far as we know, it seems to be a first example where less nucleophilic sulfoxides are more sensitive to substituent effect compared to sulfides. It is interesting to recall that sulfoxides react faster than sulfides with the same oxidant only if the sulfoxide behaves as an electrophile rather than a nucleophile and the $\rho$ value becomes positive. Because the $\rho$ value observed in the present study is negative ($\rho = -2.44$), the sulfoxides behave only as strong nucleophiles. We take these interesting results as evidence for the operation of an $S_N2$ mechanism for the oxidation of organic sulfoxides. These interesting substituent effects observed with organic sulfides and sulfoxides tempted us to postulate different mechanisms for oxidation of these two substrates. To account for the kinetic results observed with organic sulfides, a mechanism involving an electron transfer from sulfide to Mn(V) in the rate-determining step has been postulated (Scheme 1) in our earlier report.[11]

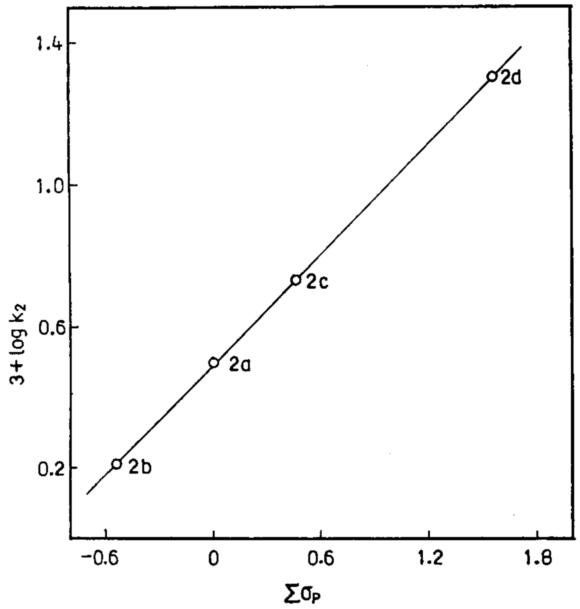


**Figure 4.** Hammett plot for the oxidation of MPSO by substituted oxo(salen)magnanese(V) complexes.

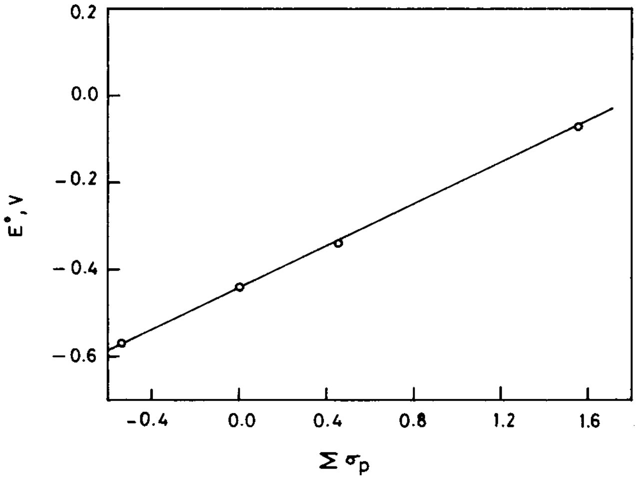


**Figure 5.** Plot of $E°$ for the Mn(II)/Mn(III) redox couple versus $\Sigma\sigma_p$ values of the substitutent in catalysts **1a**−**d**.

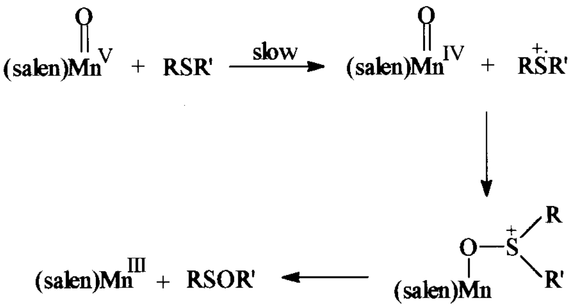
However, all arguments presented above undoubtedly support the $S_N2$ mechanism for the oxidation of aryl methyl sulfoxides by oxo(salen)manganese(V) complexes (Scheme 2). The proposed mechanism envisages the formation of intermediate I in the slow step, which then

**Table 3. Second-Order Rate Constants and $\rho$ Values for the Reactions of para-Substituted Thioanisoles ($p$-$XC_6H_4SMe$) with Substituted Oxo Complexes in Acetonitrile at 25 °C[a]**

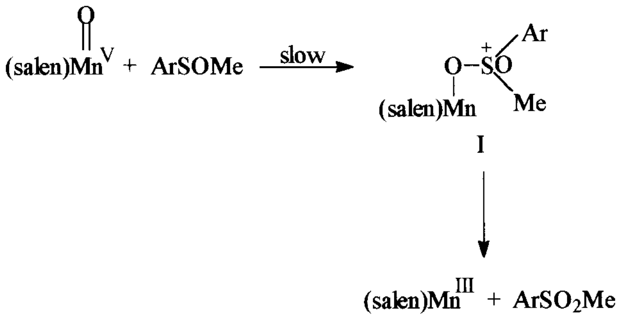
| | oxo(salen)manganese(V) complex, $10^3k_2$, $M^{-1}\ s^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| X | **2b** | **2a** | **2c** | **2d** | $\rho$ | ($r$) |
| OMe | 22.8 ± 1.2 | 26.4 ± 1.6 | 36.4 ± 2.5 | 52.0 ± 3.1 | 0.176 ± 0.042 | (0.988) |
| Me | 9.25 ± 0.40 | 12.0 ± 0.8 | 21.7 ± 1.7 | 43.6 ± 1.8 | 0.332 ± 0.075 | (0.989) |
| H | 4.37 ± 0.18 | 6.70 ± 0.39 | 14.2 ± 1.0 | 40.8 ± 3.1 | 0.474 ± 0.078 | (0.994) |
| F | 3.27 ± 0.23 | 4.89 ± 0.12 | 11.6 ± 0.2 | 30.6 ± 1.5 | 0.477 ± 0.110 | (0.989) |
| Cl | 1.73 ± 0.12 | 2.67 ± 0.29 | 8.38 ± 0.38 | 19.0 ± 1.4 | 0.515 ± 0.192 | (0.971) |
| Br | 1.48 ± 0.17 | 2.50 ± 0.11 | 7.36 ± 0.41 | 17.1 ± 0.2 | 0.520 ± 0.177 | (0.976) |
| $CO_2H$ | 0.74 ± 0.11 | 1.28 ± 0.15 | 3.46 ± 0.03 | 9.15 ± 0.12 | 0.532 ± 0.141 | (0.985) |
| COMe | 0.40 ± 0.06 | 0.71 ± 0.08 | 2.34 ± 0.04 | 4.91 ± 0.25 | 0.533 ± 0.219 | (0.965) |
| $NO_2$ | 0.12 ± 0.03 | 0.24 ± 0.04 | 0.78 ± 0.08 | 1.65 ± 0.03 | 0.554 ± 0.228 | (0.964) |
| $\rho$ | −2.06 ± 0.19 | −1.85 ± 0.16 | −1.52 ± 0.18 | −1.44 ± 0.32 | | |
| ($r$) | (0.995) | (0.995) | (0.992) | (0.970) | | |

[a] Data taken from ref 11b.

**Scheme 1**



**Scheme 2**



decomposes to give (salen)$Mn^{III}$ and sulfone as the products. The rate acceleration by electron-withdrawing groups on the 5,5′-positions of salen (**2c** and **2d**) and by the electron-donating groups in aryl methyl sulfoxides supports this formulation. The pathway proceeding through the oxametallacyclic intermediate has been excluded, because the reaction involves little steric effect when bulky methyl and phenyl groups are introduced in the 7,7′-positions (Table 1).[12b] When we look carefully at the rate constant and reaction constant ($\rho$) data collected in Tables 2 and 3, we can infer that they point out a similar mechanism for the oxo(salen)manganese(V) oxidation of organic sulfides and sulfoxides. Although less nucleophilic sulfoxides are more sensitive to substituent effect, the $k_2$ values obtained for sulfides are always 2−3 times more than the $k_2$ values observed for the corresponding sulfoxides. These data are in accordance with the Hammond postulate, i.e., consistent with a common $S_N2$ mechanism wherein only the position of the transition state changes from one substrate class to the next. The more electron-rich sulfides should have an earlier transition state for interaction with an electrophilic metal oxo complex and will thus exhibit less charge on S and a weaker influence of the substituent, leading to a low $\rho$ value. The reverse is the case with less nucleophilic substrates, with sulfoxides giving a comparatively higher $\rho$ value.[36]

To demonstrate the electrophilic nature of the oxidant and charge separation in the transition state, the influence of adding trichloroacetic acid and changing the solvent composition on the rate of oxidation of organic sulfides and sulfoxides has been studied; the data are collected in Table 4. The increase in concentration of acid, as well as the increase in the polarity of the medium, favors the rate of oxidation of sulfides and sulfoxides. The addition of acid leads to the protonation of the oxidant, and the protonated species is more electrophilic, thereby favoring the reaction. The increase in rate with the increase in the polarity of the medium points out the formation of a charge-separated transition state, which is in favor of the $S_N2$ mechanism in the oxo(salen)$Mn^V$ oxidation of organic sulfides and sulfoxides.

The oxomanganese(V) oxidation of para-substituted phenyl methyl sulfoxides 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. Although the correlation between $\Delta H^\ddagger$ and $\Delta S^\ddagger$ is not satisfactory, ($r = 0.953$), a plot of log $k_2$ at 20 °C versus log $k_2$ at 40 °C is linear ($r = 0.999$; slope $= 0.875 \pm 0.132$; $s = 0.044$), indicating that all the sulfoxides are oxidized by a similar mechanism. The enthalpy and entropy of activation for the self decay of oxo(salen)manganese(V) complex are found to be 91.0 kJ $mol^{-1}$ and −6.0 J $K^{-1}$ $mol^{-1}$, respectively.

**Reactivity−Selectivity Principle.** The observation of strong RSP in the $Mn^{III}$−salen catalyzed PhIO oxidation of organic sulfides prompted us to extend the study to organic sulfoxides. The second-order rate constants for the reactions of various para-substituted phenyl methyl sulfoxides with each of the oxo(salen)manganese(V) complexes **2a-d** are given in Table 2, and those for the organic sulfides are summarized in Table 3.

The last row of Table 2 contains $\rho$ values for substituent variation in the phenyl methyl sulfoxide for each oxo complex, and the last column shows reaction constants for substituent variation in the oxo complex for each phenyl methyl sulfoxide. The $\rho$ values in Table 2 show that there is a significant variation of reaction constants (selectivity) when we vary the nature of the substituent in either the oxo complex or the sulfoxide. Also, it is

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[36] The authors thank the referees for suggesting the application of the Hammond postulate to interpret the data with a similar $S_N2$-like mechanism for the oxidation of both substrates.

**Table 4. Effect of Adding Acid and Changing the Solvent Composition on the Rate of Oxidation of Methyl Phenyl Sulfide and Sulfoxide by 2a at 25 °C**[a,b]

| | $10^4k_1$,[c] $s^{-1}$ | | | $10^4k_1$,[d] $s^{-1}$ | |
|---|---|---|---|---|---|
| $10^2$[acid], M | sulfide | sulfoxide | $CH_3CN-H_2O$ (v/v) | sulfide | sulfoxide |
| | 6.36 ± 0.31 | 3.12 ± 0.09 | 60/40 | 110 ± 6 | 38.1 ± 1.8 |
| 1.0 | 9.71 ± 0.43 | 4.06 ± 0.14 | 70/30 | 77.6 ± 3.9 | 24.9 ± 1.3 |
| 2.0 | 21.3 ± 0.9 | 6.45 ± 0.29 | 75/25 | 63.1 ± 2.7 | 21.3 ± 0.9 |
| 5.0 | 46.5 ± 2.1 | 18.7 ± 0.8 | 80/20 | 47.9 ± 2.2 | 16.7 ± 0.5 |
| 10.0 | 148 ± 7 | 39.1 ± 1.3 | 90/10 | 30.9 ± 1.5 | 11.6 ± 0.4 |
| 40.0 | 457 ± 29 | 137 ± 8 | 100/0 | 13.4 ± 0.4 | 6.36 ± 0.21 |

[a] General conditions: [**2a**] = 0.0018 M; solvent: $CH_3CN$, unless otherwise noted. [b] In the evaluation of rate constants, the self-decomposition of **2a** at different [acid] and solvent composition is taken into account. [c] [Substrate] = 0.1 M. [d] [Substrate] = 0.2 M.

**Table 5. Second-Order Rate Constants and Activation Parameters for the Oxidation of Sulfoxides ($p$-$XC_6H_4SOCH_3$) by 2a in Acetonitrile at Four Different Temperatures**[a]

| | $10^3k_2$, $M^{-1}$ $s^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| X | 293 K | 298 K | 303 K | 313 K | $\Delta H^\ddagger$, kJ $mol^{-1}$ | $-\Delta S^\ddagger$, J $K^{-1}$ $mol^{-1}$ |
| OMe[b] | 9.26 ± 0.36 | 17.5 ± 0.4 | 24.9 ± 1.0 | 55.7 ± 1.8 | 62.5 | 69.9 |
| Me | 4.83 ± 0.13 | 7.25 ± 0.15 | 12.0 ± 0.4 | 26.1 ± 0.7 | 60.9 | 81.3 |
| H | 2.24 ± 0.08 | 3.18 ± 0.11 | 6.15 ± 0.25 | 15.3 ± 0.6 | 71.9 | 50.8 |
| Cl | 0.640 ± 0.035 | 1.21 ± 0.04 | 1.87 ± 0.07 | 5.90 ± 0.20 | 79.8 | 33.5 |
| Br | 0.465 ± 0.020 | 0.920 ± 0.050 | 1.32 ± 0.06 | 3.60 ± 0.15 | 72.0 | 62.9 |
| $NO_2$[c] | 0.020 ± 0.004 | 0.040 ± 0.004 | 0.074 ± 0.006 | 0.240 ± 0.014 | 89.8 | 28.1 |
| $\rho$ | −2.53 ± 0.48 | −2.44 ± 0.60 | −2.39 ± 0.54 | −2.21 ± 0.63 | | |

[a] General conditions: [**2a**] = 0.0018 M; [sulfoxide] = 0.2 M. [b] [Sulfoxide] = 0.1 M. [c] [Sulfoxide] = 0.5 M.

**Table 6. Results of Correlation between log $k_{Fi}$ and log $k_{Si}$ According to eq 4 for Aryl Methyl Sulfoxides**

| | oxo(salen)manganese(V) complexes (F and S) | | | | | |
|---|---|---|---|---|---|---|
| results | **2a** and **2b** | **2c** and **2b** | **2c** and **2a** | **2d** and **2b** | **2d** and **2a** | **2d** and **2c** |
| $r$ | 0.997 | 0.991 | 0.998 | 0.983 | 0.993 | 0.996 |
| $b$ | 0.912 ± 0.078 | 0.852 ± 0.182 | 0.937 ± 0.056 | 0.664 ± 0.198 | 0.733 ± 0.142 | 0.784 ± 0.110 |
| $\Delta$ | 0.280 | 0.518 | 0.238 | 1.05 | 0.773 | 0.535 |

apparent that as the reactivity of either sulfoxide or oxo complex decreases, the $\rho$ value increases, i.e., there is an inverse relationship between reactivity and selectivity in both cases. These results are very similar to those observed with aryl methyl sulfides (Table 3).[11]

Hence, we have attempted to analyze the data by applying a method formulated by Exner[37] to verify the operation of RSP. Accordingly, the rate data reported in Table 2 were subjected to mathematical treatment using eqs 4 and 5.

$$\log k_{Fi} = a + b \log k_{Si} + \varepsilon_i \qquad (4)$$

$$\Delta = (\sum_i \log k_{Fi} - \sum_i \log k_{Si})/N \qquad (5)$$

where $k_{Fi}$ and $k_{Si}$ are the second-order rate constants for the reactions of fast and slow reagents (oxo complexes), respectively, with each sulfoxide, $\varepsilon_i$ is the error of the log $k_{Fi}$ versus log $k_{Si}$ correlation, and $\Delta$ is the mean difference. The values of $b$ and $\Delta$ were calculated for all of the six possible combinations of one fast and one slow reagent (among the four oxo complexes) with a series of similar substrates (six sulfoxides). The results summarized in Table 6 show a valid RSP in all cases as the value of $b$ is less than unity and $\Delta$ is not too small.

In a system involving more than one reagent and the same set of substrates, the existence of a "magic point"[37] in the log $k_{Fi}$ versus log $k_{Si}$ plots is an indication for a strong RSP. The magic point represents some limiting value of reactivity in which, for a particular substrate, the reaction rate is independent of the reagent and vice versa. In this aspect, the present system reveals interesting results (Figure 6). The correlations involving nitro-substituted oxo complex **2d** (lines d-f) produce one magic point, $y_o(1)$, and the correlations involving other oxo complexes (lines a-c) produce another magic point, $y_o(2)$.

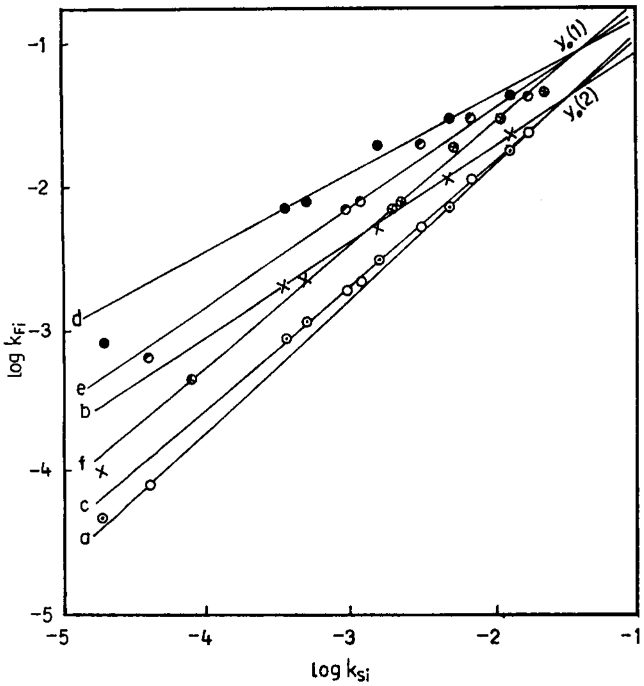

**Figure 6.** Log $k_{Fi}$ versus log $k_{Si}$ plot for the reactions of aryl methyl sulfoxides with (a) **2a** and **2b**, (b) **2c** and **2b**, (c) **2c** and **2a**, (d) **2d** and **2b**, (e) **2d** and **2a**, and (f) **2d** and **2c**.

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(37) Exner, O. *J. Chem. Soc., Perkin Trans 2* **1993**, 973.

Both magic points are situated on the side of high reactivity, as expected for a strong RSP as observed in the solvolysis[37,38] of various meta- and para-substituted allyl benzensulfonates with various alcohols and oxo-(salen)manganese(V) oxidation of organic sulfides.[11] The fact that the present system obeys RSP may be considered as evidence that the same mechanism is operating in all reactions.

## Experimental Section

**Materials.** All the aryl methyl sulfoxides were prepared from the corresponding sulfides according to the literature procedure.[39] All the sulfoxides were purified by vacuum distillation/recrystallization from suitable solvents. The physical constants of the sulfoxides were found to agree with literature values.[39] The HPLC analyses of each sulfoxide showed the presence of a single entity, and no impurity peak appears in the $^1$H NMR spectra. Acetonitrile (GR, E. Merck) was first refluxed over $P_2O_5$ for 5 h and then distilled. Iodosylbenzene was prepared from (diacetoxyiodo)benzene by a standard method.[40]

The $[Mn^{III}(salen)]^+PF_6^-$ complexes were synthesized according to a known procedure.[11a,13] The IR and UV−vis spectral studies of all of the complexes were found to be identical with literature data.[13] The oxo complexes **2a-f** were generated[11a] in situ by stirring magnetically 0.15 mmol of finely powdered PhIO in 5 ml of an acetonitrile solution containing 0.015 mmol of the corresponding $Mn^{III}$(salen) complex for 5 min under nitrogen, followed by filtration at ice temperature to remove the undissolved iodosylbenzene. The conversion of $Mn^{III}$ to $Mn^V$ may be considered quantitative in the sense that prolonged stirring causes no change in the initial absorption spectrum of the $Mn^V$ solution. Because the oxomanganese(V) complex undergoes autodecomposition, the solutions were prepared freshly for each kinetic run.

**Kinetic Measurements.** Reaction mixtures for kinetic runs were prepared by quickly mixing the solutions of the oxo complex and the sulfoxide in varying volumes so that in each run the total volume was 5 ml. The kinetics was followed in a Perkin-Elmer UV−vis spectrophotometer (Lambda 3B) fitted with a thermostated cell compartment under pseudo-first-order conditions ([sulfoxide] > [oxo complex]) in acetonitrile at 25 ± 0.1 °C by monitoring the decay of the oxo complex at 680 nm.[11a,13]

The rate constants were computed from the linear least-squares plots of $\log(A_t - A_\infty)$ versus time, where $A_t$ is the absorbance at time $t$ and $A_\infty$ is the experimentally determined infinity point. The first-order rate constants $k_{1(dec)}$ for the autodecomposition of oxomanganese(V) were determined from the first-order plots up to 50−60% of reaction. The plots for the decay of the oxo complex in the presence of sulfoxide were linear over 20% of reaction, and the pseudo-first-order rate constants $k_{1(obs)}$ were determined from the disappearance of the oxo complex up to this extent. The values of $k_1$ were obtained[11,41] as $k_1 = k_{1(obs)} - k_{1(dec)}$. The second-order rate constants were obtained by the relation $k_2 = k_1$/[sulfoxide].

**Product Analysis.** The reaction mixture from an actual kinetic run was subjected to vacuum evaporation, and the residue was then extracted with diethyl ether. The ethereal extract was dried over anhydrous $Na_2SO_4$, and the solvent was evaporated. The product was dissolved in $CH_2Cl_2$, and GC analyses of the samples showed the presence of sulfone and iodobenzene. The yield of sulfone (75−94%) depended on the sulfoxide and oxo complex employed. The lower yield of sulfone may be attributed to the competitive self-decomposition of the oxomanganese(V) complex to the $Mn^{III}$ complex, which is confirmed by the near quantitative recovery of $Mn^{III}$ complex from the reaction mixture.

**Stoichiometry.** To determine the stoichiometry, the reaction was carried out under the experimental conditions ([**2**] = 0.0018 M; [PhSOMe] = 0.2 M). The resultant solution after the completion of the reaction gave sulfone in ca. 79% yield and $Mn^{III}$(salen) complex in ca. 95% yield. Accordingly, the stoichiometry of the reaction can be represented by eq 6.

$$O{=}Mn^V(salen)^+ + PhSOMe \rightarrow Mn^{III}(salen)^+ + PhSO_2Me \quad (6)$$

**Acknowledgment.** We thank CSIR, New Delhi, for providing financial assistance in the form of a project. P.K. thanks the U.G.C., New Delhi, and Manonmaniam Sundaranar University, Tirunelveli, for an award of a Fellowship under FIP. He also thanks the Principal and Management of Sri K.G.S. Arts College, Srivaikuntam, for granting permission to accept the fellowship.

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