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Electronic and Steric Effects on the Oxygenation of Organic Sulfides and Sulfoxides with Oxo(salen)chromium(V) Complexes

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The kinetics of oxygenation of several *para*-substituted phenyl methyl sulfides and sulfoxides with a series of 5-substituted and sterically hindered oxo(salen)chromium(V) complexes have been studied by a spectrophotometric technique. Though the reaction of sulfides follows simple second-order kinetics, sulfoxides bind strongly with the metal center of the oxidant and the oxygen atom is transferred from the oxidant−sulfoxide adduct to the substrate. The reduction potentials, E_{red}, of eight Cr(V) complexes correlate well with the Hammett σ constants, and the reactivity of the metal complexes is in accordance with the E_{red} values. The metal complexes carrying bulky *tert*-butyl groups entail steric effects. Organic sulfides follow a simple electrophilic oxidation mechanism, and the nonligated sulfoxides undergo electrophilic oxidation to sulfones using the oxidant−sulfoxide adduct as the oxidant. Sulfoxides catalyze the Cr(V)−salen complexes' oxygenation of organic sulfides, and the catalytic activity of sulfoxides is comparable to pyridine *N*-oxide and triphenylphosphine oxide. The rate constants obtained for the oxidation of sulfides and sulfoxides clearly indicate the operation of a pronounced electronic and steric effect in the oxygenation reaction with oxo(salen)chromium(V) complexes.

Introduction

To establish the nature of the reactive intermediates and the mechanism of enzyme-catalyzed oxygenation of biological substrates, extensive studies have been carried out using synthetic metal−porphyrins as model compounds.[1−4] Apart from porphyrins, the tetradendate ligand salen (*N*,*N*′-bis(salicylidine)ethylenediaminato) has been chosen by many workers[5−9] for the following reasons: (i) unlike porphyrins, it is relatively easy to synthesize a large variety of salens from readily available precursors, by the condensation of derivatives of salicylaldehyde and ethylenediamine, (ii) the introduction of stereogenic centers near the coordinated metal makes the transmission of the stereochemical information more feasible, (iii) the phenolate group mimics the tyrosinate moiety present in biological systems, while the imine functionality provides some correspondence with the postulated imidazole binding in the enzymes, and (iv) the electronic and steric effects of oxo(salen)metal complexes can be finely tuned by introducing suitable substituents in 3- and 5-positions of the salen ligand. Further, the Cr(V)−salen complex chosen for the present study mimics Cr−peptide complexes that may form upon intracellular reduction of Cr(VI) by virtue of the mixed nitrogen and oxygen ligand chelation.[10]

Though Cr(VI) is an excellent reagent to carry out oxidation and has been extensively used for the oxidation of a variety of organic compounds, it is carcinogenic.[11−21]

(1) Meunier, B., Ed. *Biomimetic Oxidations Catalyzed by Transition Metal Complexes*; Imperial College Press: London 2000.
(2) Sheldon, R. A., Ed. *Metalloporphyrins in Catalytic Oxidations*; Marcel Dekker: New York, 1994. (b) Montarari, F., Casella, L., Eds.; *Metalloporphyrins Catalyzed Oxidation*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1994.
(3) Brothers, P. J. In *Advances in Organometallic Chemistry*; Stone, F. C. A., West, R., Eds.; Academic Press: New York, 2001; Vol 46, p 264.
(4) Holm, R. K.; Kennepohl, P.; Solomon, E. I. *Chem. Rev.* **1996**, *96*, 2239 and the subsequent articles appearing in the issue.
(5) (a) Canali, L.; Sherrington, D. C. *Chem. Soc. Rev.* **1999**, *28*, 85 and references therein. (b) Atwood, D. A.; Harvey, M. J. *Chem. Rev.* **2001**, *101*, 37.
(6) Jacobsen, E. N. *Acc. Chem. Res.* **2000**, *33*, 421.
(7) (a) Katsuki, T. *Coord. Chem. Rev.* **1995**, *140*, 189. (b) Ito, Y. N.; Katsuki, T. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 603.
(8) Jacobsen, E. N. In *Comprehensive Organometallic Chemistry II*; Wilkinsen, G., Stone, F. G. A., Abel, E. W., Hegedus, L. S., Eds.; Pergamon: New York, 1995; Vol.12, Chapter 11.
(9) Bandini, M.; Cozzi, P. G.; Umani-Ronchi, A. *Chem. Commun.* **2002**, 919.
(10) Sugden, K. D.; Campo, K. C.; Martin, B. D. *Chem. Res. Toxicol.* **2001**, *14*, 1315.
(11) (a) Wiberg, K. B. *Oxidation in Organic Chemistry*; Academic Press: New York, 1965. (b) Benson, D. *Mechanism of Oxidation by Metal Ions*; Elsevier: New York, 1976.
(12) Kochi, J. K. *Metal-Catalysed Oxidation of Organic Compounds*; Academic: New York, 1981.
(13) Connett, P. H.; Wetterhahn, K. E. *J. Am. Chem. Soc.* **1985**, *107*, 4282.
(14) Lay, P. A.; Levina, A. *Inorg. Chem.* **1996**, *35*, 7709.
(15) (a) Perez-Benzito, J. F.; Lamrhari, D.; Arias, C. *J. Phys. Chem.* **1994**, *98*, 12621. (b) Perz-Benito, J. F.; Arias, C.; Rodriquez, R. M.; Ros, M. *New J. Chem.* **1998**, 1445.
(16) Barr-David, G.; Charara, M.; Codd, R.; Farrell, R. P.; Irivin, I. A.; Lay, P. A.; Bramley, R.; Brumby, S.; Ji, J. Y.; Hanson, G. R. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1207.
(17) Farrell, R. P.; Lay, P. A. *Comments Inorg. Chem.* **1992**, *13*, 133.
(18) Gould, E. S. *Acc. Chem. Res.* **1986**, *19*, 66.
(19) Sugden, K. D.; Wetterhahn, K. E. *Chem. Res. Toxoicol.* **1997**, *10*, 1397.

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It has been proposed[16−22] that one of the intermediate species responsible for the carcinogenicity of chromium is Cr(V). Recently Cr(III)−salen complexes have been proved to be extremely good catalysts for many redox processes.[6,9,23−25] In a recent report, Jacobsen and coworkers,[26] in the case of a Mn(III)−salen-catalyzed epoxidation reaction, have established that the electron-donating substituents on the ligand lead to higher levels of asymmetric induction, while electron-withdrawing substituents decrease the enantioselectivity. The authors have suggested that these effects may be interpreted according to the Hammond postulate, wherein ligand substituents influence enantioselectivity by modulating the reactivity of the high-valent oxo(salen)manganese-(V) ion. Although manganese and chromium oxo salen complexes share similarities, there exists substantial differences in the characteristics of the two reagents.[27] The stoichiometric variant of the chromium system can easily be studied, since the oxo(salen)chromium(V) ion is isolable, whereas oxo(salen)manganese(V) has fleeting existence. The major difference between these two metal complexes is in their different substrate selectivity, particularly in the asymmetric epoxidation. The O-donor ligand additives have greater effect with Cr complexes compared to Mn. The success of these metal−salen systems has led to considerable discussion of the mechanism of oxo transfer and the origin of enantioselectivity.[27]

In a recent report from our laboratory,[28] we have proved that oxo(salen)chromium(V) complexes oxidize organic sulfides selectively to sulfoxides and the yield of sulfoxide is excellent. When we extend our study to the next stage of oxidation, sulfoxides to sulfones, interestingly sulfoxides bind with oxo(salen)chromium(V) ion and the absorption maximum, λ_{max}, of Cr(V) shifts from 560 to 606 nm and the peak sharpens (*vide infra*).

From the spectral studies we understand that DMSO and aryl methyl sulfoxides bind with all Cr(V)−salen complexes. Interestingly, the bound sulfoxides act as donor ligands to catalyze the oxidation of organic substrates. Herein we report the results obtained from a detailed analysis of the electronic and steric effects by introducing electron-donating and -withdrawing groups and bulky *tert*-butyl groups in the 3,3′- and 5,5′-positions of the salen ligand of oxo(salen)chromium(V) ion and by changing the salen to salophen and cyclosalen on the oxidation of several aryl methyl sulfides and sulfoxides. As the donor ligands such as pyridine *N*-oxide and triphenylphosphine oxide catalyze the oxygenation reaction of oxo(salen)metal complexes, we have checked the catalytic role of MPSO on the oxometal ion oxidation of organic sulfides.

Results and Discussions

As far as Cr(III)−salen complexes are concerned, it has been well-established that oxo(salen)chromium(V) complexes are formed when PhIO is used as the oxidant.[28,29] Further, these reactive oxo(salen)chromium(V) complexes are stable, particularly in nonaqueous solvents such as CH_3CN, and well characterized by spectral techniques and X-ray analysis.[29] This is the advantage of Cr(V)−salen complexes compared to the corresponding Mn(V) and Fe(V) complexes, which are less stable under present experimental conditions. Therefore, in the present study the oxo(salen)chromium(V) complexes **IIa**−**IIj** have been synthesized from Cr(III)−salen complexes **Ia**−**Ij** and PhIO (Chart 1) and then used for the oxygenation of organic sulfides and sulfoxides. The formation of oxometal ion is confirmed from the absorption spectra of complexes **IIa**−**IIj**, which are similar to those of the previous reports and from mass spectral studies.[6,9,24,25,29]

The absorption maximum of oxo(salen)chromium(V) ion is sensitive to the nature of substituents at 5,5′-positions of the salen ligand. The parent complex has the maximum absorption at 560 nm. The presence of an electron-donating group, 5-Me, slightly blue shifts the λ_{max} from 560 to 557 nm, and the electron-withdrawing groups red shift the λ_{max} to 584 (5-Cl) and 590 nm (5-Br). The absorption maxima of Cr(III)−salen and oxo(salen)chromium(V) complexes are collected in Table 1.

The kinetics of oxidation of several aryl methyl sulfides and sulfoxides with oxo(salen)chromium(V) complexes **IIa**−**IIj** has been followed in CH_3CN by a spectrophotometric technique under pseudo-first-order conditions in the presence of excess substrate over Cr(V). The rate of PhIO oxidation of the organic substrates has been checked and found to be very slow under the present experimental conditions.

Electrochemical Properties of Oxo(salen)chromium(V) Complexes. The cyclic voltammograms of eight oxo(salen)chromium(V) complexes were recorded, and the reduction potential values in CH_3CN are collected in Table 1.

The voltammogram of complex **IIa**, which is quasireversible, is shown in Figure 1. From the data collected in Table 1, we understand that the reduction potential value is susceptible to the nature of substituent in the salen ligand. The E_{red} values of oxo(salen) chromium(V) complexes with 5,5′-substituted electron-donating and -withdrawing groups in the salen ligand correlate well with the Hammett substituent constant and the slope from the plot is 0.29 (see Supporting Information, Figure

(20) Levina, A.; Bailey, A. M.; Champion, G.; Lay, P. A. *J. Am. Chem. Soc.* **2001**, *122*, 6208.
(21) Codd, R.; Dillion, T. C.; Levia, A.; Lay, P. A. *Coord. Chem. Rev.* **2001**, *216*, 5371.
(22) (a) Vincent, J. B. *Acc. Chem. Res.* **2000**, *33*, 503. (b) Vincent, J. B. *Polyhedron* **2001**, *20*, 1.
(23) Zhou, X.-G.; Yu, X.-Q.; Huong, J- S.; Li, S.-G.; Li, L.-S.; Che, C.-M. *Chem. Commun.* **1999**, 1789.
(24) Paddock, R. L.; Nguyen, S. T. *J. Am. Chem. Soc.* **2001**, *123*, 11498.
(25) (a) Dalton, C. T.; Ryan, K. M.; Wall, V. M.; Bousquet, C.; Gilhenay, D. G. *Top. Catal.* **1998**, *5*, 71. (b) O'Mahony, C. P.; McGarrigle, E. M.; Renehan, M. F.; Ryan, K. M.; Kerrign, N. J.; Bousquet, C.; Gilheany, D. G. *Org. Lett.* **2001**, *22*, 3435. (c) Daly, A. M.; Renehan, M. F.; Gilheany, D. G. *Org. Lett.* **2001**, *5*, 663. (d) Kerrigan, N. J.; Langan, I. J.; Dalton, C. T.; Daly, A. M.; Bausquet, C.; Gilheany, D. G *Tetrahedron Lett.* **2002**, *43*, 2107. (e) Dalton, C. T.; Ryan, K. M.; Langan, I. J.; Coyne, E. J.; Gilheany, D. G. *J. Mol. Catal. A: Chem.* **2002**, *187*, 179. (f) Daly, A. M.; Gilheany, D. G. *Tetrahedron: Asymmetry* **2003**, *14*, 127.
(26) Palucki, M.; Finney, N. S.; Pospisil, P. J.; Guler, M. L.; Ishida, T.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1998**, *120*, 948.
(27) (a) Brandt, P.; Norrby, P.; Daly, A. D.; Gilheany, D. G. *Chem. Eur. J.* **2002**, *8*, 4299. (b) Cavallo, L.; Jacobsen, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 589. (c) Abashkin, Y. G.; Collins, J. R.; Burt, S. K. *Inorg. Chem.* **2001**, *40*, 4040.
(28) Sevvel, R.; Rajagopal, S.; Srinivasan, C.; Alhaji, N. M. I.; Chellamani, A. *J. Org. Chem.* **2000**, *65*, 3334.
(29) (a) Samsel, E. G.; Srinivasan, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 7606. (b) Srinivasan, K.; Kochi, J. K. *Inorg. Chem.* **1985**, *24*, 4671.

CHART 1

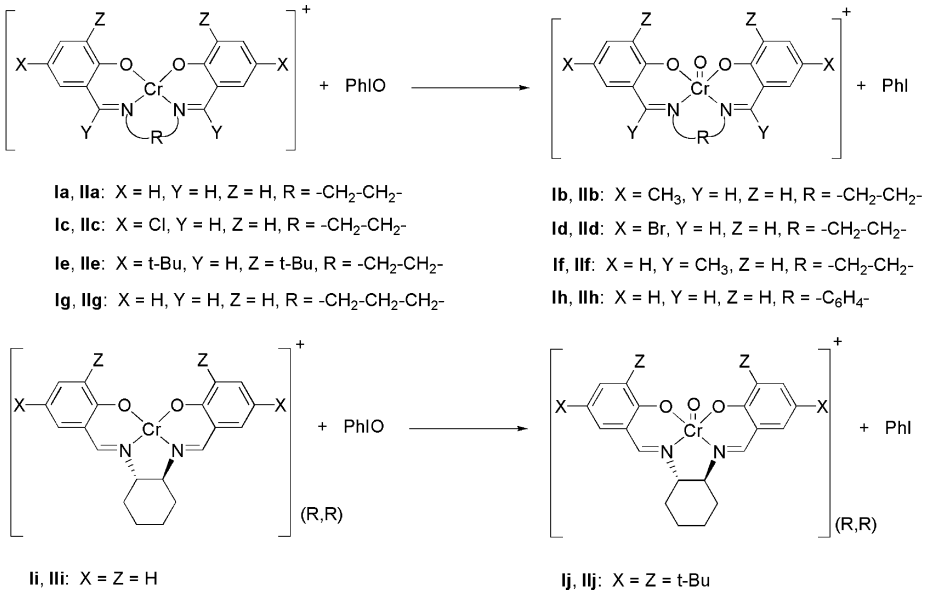


TABLE 1. Absorption Maxima, Redox Potentials, and Binding Constant (K_f) Values of Cr^{III}−Salen Ia−Ij and Oxo(salen)chromium(V) Complexes IIa−IIj

			λ_{max} for oxo(salen)chromium ion			
ligand	λ_{max} for Cr^{III}−salen	E_{red}, mV	without additive	with MPSO	with DMSO	K_f, M^{-1}
salen	361, 415	441	560	606	603	12.5
5-Me(salen)	338, 429	406	557	610	615	17.5
5-Cl(salen)	350, 426	601	584	622	625	148
5-Br(salen)	346, 424	609	590	625	630	137
3,5-di-*t*-Bu(salen)	358, 427	239	595	660	668	8.4
7,7-dimethyl(salen)	412, 494		610	640	645	
salprn	376, 420		570	605	610	11.5
cyclo(salen)	356, 425	446	600	610	615	134
salophen	376, 420	611	600	620	625	42.4
3,5-di-*t*-Bu-cyclo(salen)	354, 430	224	610	660	675	10.9

S1). At this juncture it is of interest to compare the electrochemical stability of oxo(salen)chromium(V) complexes with the corresponding iron and manganese complexes. The CV of oxo(salen)iron(V) and manganese(V) complexes could not be recorded, as they are electrochemically unstable, and the CV data obtained for M(III)−salen complexes (M = Fe, Mn) have been used for the analysis of kinetic data. The CV recorded for oxo(salen)chromium(V) complexes confirms the greater stability of oxo(salen)chromium(V) complexes compared to Fe and Mn complexes.

The reactivity of oxo(salen)chromium(V) complexes toward organic sulfides and sulfoxides is in accordance with reduction potential values of the complexes (*vide infra*). The electron-withdrawing substituents on the salen ligand lead to higher reduction potentials, making them more powerful oxidants compared to the parent complex, and the presence of electron-donating substituents such as Me and *tert*-butyl entails low reduction potentials, thereby attenuating the reactivity, and thus act as relatively less powerful oxidants. Since we are able to measure the reduction potentials of oxo(salen)chromium(V) complexes, the change of electrophilicity of the oxidant with the change of substituents in the salen ligand is clearly verified in the oxo(salen)chromium(V) complexes. In our previous studies with oxo(salen)iron and oxo(salen)manganese complexes, we could not verify this because of the lower stability of these complexes.[30,31]

Oxidation of Organic Sulfides. The results on the oxygenation of organic sulfides with four oxo(salen)chromium(V) complexes (**IIa**, **IIf**, **IIg**, and **IIh**) have already been reported from this laboratory.[28] To understand the role of electronic and steric effects on this selective oxidation reaction, we have synthesized six more Cr(V) complexes, two of them carrying a chiral center, and used them for the selective oxidation of organic sulfides. The reaction is highly sensitive to the change of the substituents in the salen ligand, and the results observed from the kinetic, spectral, and product analysis studies are presented here. The kinetic data for the reaction have been obtained by measuring the change in OD with time, and a sample run is given in the Supporting Information (Figure S2). The Cr(V) oxidation of organic sulfides is first-order with respect to all Cr(V) complexes, which is evident from the linear log OD vs time plot. The reaction is also first-order with respect to sulfide, and

(30) Chellamani, A.; Alhaji, N. M. I.; Rajagopal, S.; Sevvel, R.; Srinivasan, C. *Tetrahedron*. **1995**, *51*, 12677. (b) Chellamani, A.; Alhaji, N. M. I.; Rajagopal, S. *J. Chem. Soc., Perkin Trans. 2* **1997**, 299.

(31) Sivasubramanian, V. K.; Ganesan, M.; Rajagopal, S.; Ramaraj, R. *J. Org. Chem*. **2002**, *67*, 1506. (b) Sivasubramanian, V. K. Ph.D. Thesis, Madurai Kamaraj University, 2002.

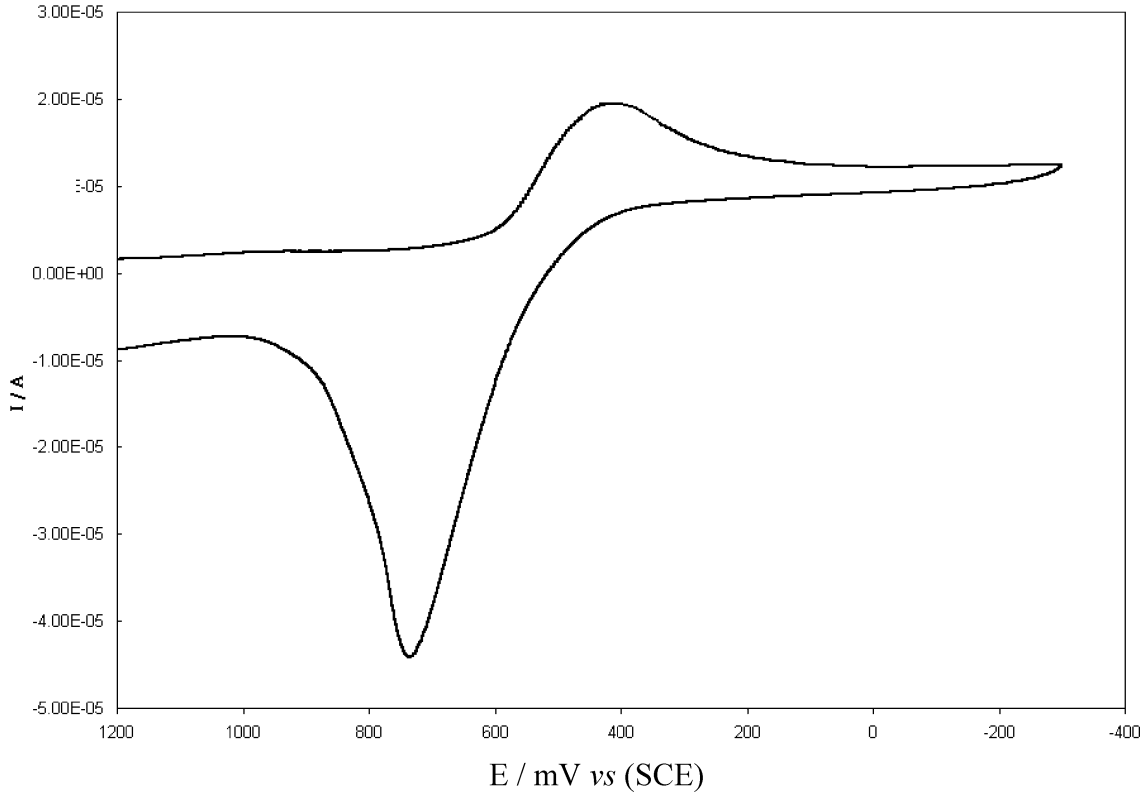


FIGURE 1. Cyclic voltammogram of **IIa** in CH_3CN.

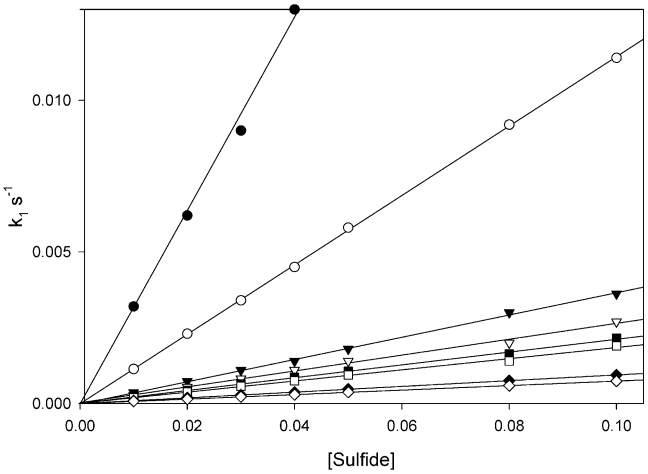


FIGURE 2. Plot of k_1 vs [sulfide] for the reaction of *p*-XC_6H_4-SMe with **IIb**: ●, *p*-OMe; ○, *p*-Me; ▼, H; ▽, *p*-F; ■, *p*-Cl; □, *p*-Br; ◆, *p*-COOH; ◇, *p*-$COCH_3$.

this is confirmed from the linear k_1 vs [sulfide] plots shown in Figure 2 and the constant k_2 value.

Similar results are observed for the oxidation of all substituted phenyl methyl sulfides with 10 oxo(salen)-chromium(V) complexes. The addition of sulfide to the oxidant does not show any noticeable shift in the λ_{max} value and increase in the OD, indicating that there is no complex formation or binding of substrate with the oxidant prior to the rate-controlling step of the oxidation reaction. This observation is in striking contrast to our recent report on the oxygenation of organic sulfides with oxo(salen)iron complexes, where the substrate binds with the oxidant and the reaction follows Michaelis−Menten kinetics with respect to the substrate, sulfide.[31]

Substituent Effects. The data provided in Table 2 point out that the redox reaction between oxo(salen)-chromium(V) complexes and organic sulfides is highly sensitive to the introduction of substituents in the aryl moiety of aryl methyl sulfides and in the 3,3′- and 5,5′-positions on the salen ligand.

The introduction of substituents in the para-position of the phenyl ring of PhSMe alters the rate appreciably; i.e., the electron-donating substituents accelerate the rate and electron-withdrawing groups decelerate it. The kinetic data have been treated with the Hammett equation, and the plot of log k_2 vs Hammett σ constants is linear (Figure 3)[32] in all 10 complexes **IIa**−**IIj**. The reaction constant value, ρ, is negative and the ρ values fall in the range of −1.1 to −2.8, for substituted oxo(salen)chromium(V) complexes.

The ρ value for the reaction of sulfides with each of the oxo complexes is given at the bottom of Table 2. The negative ρ value indicates that positive charge is developed on the sulfur center of the substrate in the transition state. The introduction of a substituent in the salen ligand also alters the rate of the reaction substantially; the observed kinetic data are analyzed in terms of the Hammett equation, and the ρ value is positive. The ρ values for the substituent variations in the oxo complexes for each sulfide are given in the seventh column of Table 2 and the value is in the range from 2.2 to 2.6. This ρ value is high compared to other metal−salen complexes

(32) The sulfide containing *p*-COOH is not included in this Hammett, as the addition of this sulfide shifts the λ_{max} of oxo(salen)-chromium(V) ion to the tune of 5 nm, indicating that the carboxylate group may be coordinated to the metal, thereby enhancing the reactivity of the oxidant. The catalytic activity of carboxylic acids on the reaction of oxo(salen)chromium(V) ion has been explained in the previous report.

TABLE 2. Second-Order Rate Constant, k_2, Values for Oxidation of *p*-XC_6H_4SMe with Oxo(salen)chromium(V) Complexes IIa−IIj in CH_3CN at 298 K

	$k_2 \times 10^3$ M^{-1} s^{-1}										
X	**IIa**	**IIb**	**IIc**	**IId**	**IIe**	ρ (r)	**IIf**	**IIg**	**IIh**	**IIi**	**IIj**
H	1.31 ± 0.03	1.15 ± 0.04	36.4 ± 0.9	45.8 ± 1.4	0.110 ± 0.00	2.2 (0.980)	1.11 ± 0.21	9.30 ± 0.20	29.4 ± 0.5	1.20 ± 0.03	0.189 ± 0.010
OMe	25.9 ± 0.59	4.60 ± 0.13	320 ± 9.6	526 ± 14	0.360 ± 0.01	2.6 (0.995)	6.81 ± 0.62	62.0 ± 2.9	111 ± 4.0	5.10 ± 0.15	0.368 ± 0.010
Me	11.4 ± 0.23	2.60 ± 0.52	114 ± 2.4	140 ± 4.2	0.170 ± 0.00	2.4 (0.988)	2.32 ± 0.25	19.9 ± 0.6	56.1 ± 0.1	2.20 ± 0.06	0.276 ± 0.000
F	1.58 ± 0.08	0.59 ± 0.10	26.9 ± 0.4	61.0 ± 1.3	0.063 ± 0.00	2.4 (0.995)	0.95 ± 0.19	6.2 ± 0.2	31.6 ± 0.2	1.10 ± 0.04	0.146 ± 0.000
Cl	0.93 ± 0.01	0.32 ± 0.01	21.6 ± 0.4	43.8 ± 1.0	0.058 ± 0.00	2.4 (0.995)	0.57 ± 0.03	3.25 ± 0.11	20.5 ± 0.5	0.65 ± 0.02	0.128 ± 0.000
Br	0.93 ± 0.01	0.28 ± 0.06	18.8 ± 0.8	24.2 ± 0.4	0.038 ± 0.00	2.4 (0.998)	0.56 ± 0.03	3.33 ± 0.05	20.6 ± 0.5	0.42 ± 0.01	0.090 ± 0.000
CO_2H	0.24 ± 0.02	0.25 ± 0.01	9.40 ± 0.2	6.70 ± 0.13	0.017 ± 0.00	2.2 (0.970)	0.19 ± 0.03	1.26 ± 0.04	13.0 ± 0.6	0.21 ± 0.01	0.062 ± 0.010
$COCH_3$	0.16 ± 0.01	0.23 ± 0.01	7.40 ± 0.2	8.80 ± 0.15	0.014 ± 0.00	2.3 (0.965)	0.12 ± 0.03	1.06 ± 0.06	12.0 ± 0.4	0.22 ± 0.00	0.061 ± 0.000
ρ	−2.8	−1.9	−2.0	−2.2	−1.8		−2.1	−2.3	−1.2	−1.8	−1.1
R	0.965	0.980	0.972	0.953	0.970		0.975	0.992	0.976	0.988	0.990

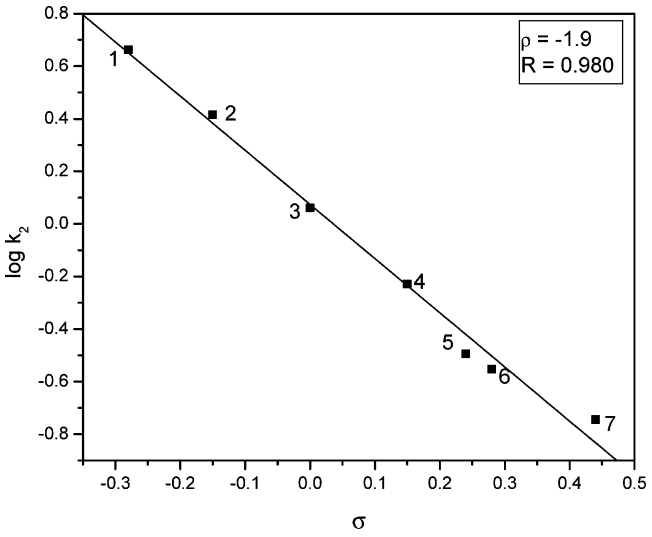


FIGURE 3. Hammett plot for the oxidation of *p*-XC_6H_4SMe with **IIb**: 1, *p*-OMe; 2, *p*-Me; 3, H; 4, *p*-F; 5, *p*-Cl; 6, *p*-Br; 7, *p*-$COCH_3$.

used for the oxidation of organic sulfides,[30,31] and it shows the development of negative charge on the oxidant in the transition state. It is interesting to compare the results observed here with those obtained with oxo(salen)iron and oxo(salen)manganese complexes on the oxygenation of organic sulfides. With the iron complexes the ρ values observed for the substituent variations in the oxidant and substrate are 0.8 and −1.5, respectively,[31] and for the oxo(salen)manganese complexes the corresponding ρ values are 0.5 and −1.8, respectively.[30] This comparison points out that among the oxo metal−salen complexes used so far for the oxidation of organic substrates, Fe, Mn, and Cr, the Cr(V) complexes are the most stable and the oxygenation reaction is more sensitive to the change of substituents in the oxidant and the substrate.

Steric Effect. To realize the role of the steric effect in this reaction, we have synthesized oxo(salen)chromium(V) complexes with bulky *tert*-butyl group in the 3- and 3′-position along with the 5- and 5′- positions of salen ligand (complexes **IIe** and **IIi**) and used them to study the kinetics of the oxygenation reaction. When we compare the kinetic data observed for complexes **IIa**, **IIe**, **IIi**, and **IIj**, the k_2 values for **IIa** and **IIi** are more than 1 order higher than the values obtained for **IIe** and **IIj**, respectively. It is important to remember that *tert*-butyl is an electron-donating substituent and the σ value is −0.15. Hence, it is appropriate to compare the behavior of complexes **IIb** and **IIe**. Though both of them contain electron-donating substituents, the k_2 values observed with the latter is 1 order less than the former. Thus from the comparison of kinetic data observed with the Cr(V) complexes **IIa**, **IIb**, and **IIe**, we understand that the presence of a *tert*-butyl group in the 3,3′-positions leads to enormous retardation in the rate, implying the importance of the steric effect in this reaction. We arrive at a similar conclusion when we compare the kinetic data observed with **IIi** and **IIj**.

Selective Oxidation of Organic Sulfide to Sulfoxide. The selective oxidation of organic sulfide to sulfoxide is of importance, particularly in the preparation of chiral sulfoxides, which are used as the starting materials in the synthesis of a variety of chiral organic molecules.[33] In the case of metal−salen complexes, the transfer of chirality to the substrate has been well-established, particularly for the epoxidation and sulfoxidation reactions.[34] At this stage, it is useful to compare the reactivity of Cr−salen and Mn−salen complexes toward sulfides under similar reaction conditions. The ρ value is high (−2.8) with Cr(V)−salen oxidation of organic sulfides compared to Mn(V)−salen oxidation (−1.9), and the transition state is more product-like, with Cr(V) complexes leading to more selective formation of sulfoxide. A relatively late transition state suggests a strong interaction of incoming sulfide with the metal complex. The data given in Table 3 show that the percentage conversion for sulfide to sulfoxide is highly sensitive to the nature of the substituents in the phenyl ring of PhSMe and the structure of Cr(V)−salen complexes.

In the present study, we show that the Cr(V) complexes carrying a chiral center also leads to selective oxidation of sulfides to sulfoxides. However, at this stage we are not reporting the value of the enantiomeric excess (ee) of sulfoxide formed. The detailed study on the synthetic utility of this redox system for the synthesis of chiral sulfoxides and percentage of enantiomeric excess (ee) of sulfoxide formed will be reported separately.

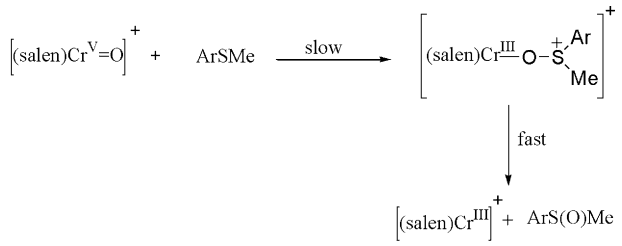
Mechanism of Sulfide Oxidation. The kinetic results observed in the present study with oxo(salen)-chromium(V) complexes carrying electron-donating and -withdrawing substituents in the salen ligand and sub-

(33) Carreno, M. C. *Chem. Rev.* **1995**, *95*, 1717.
(34) (a) Tanaka, R.; Saito, B.; Katsuki, T. *Tetrahedron Lett.* **2002**, *43*, 3259. (b) Saito, B.; Katsuki, T. *Tetrahedron Lett.* **2001**, *42*, 3873. (c) Saito, B.; Katsuki, T. *Tetrahedron Lett.* **2001**, *42*, 8333. (d) Adam, W.; Fell, R. T.; Stegmann, V. R.; Saha-Moller, C. R. *J. Am. Chem. Soc.* **1998**, *120*, 708.

TABLE 3. Percentage of Sulfoxide Formed from the Selective Oxidation of *p*-X-C_6H_4-S-CH_3 with IIa, IIg, IIh, IIi, and IIj in CH_3CN at 298 K

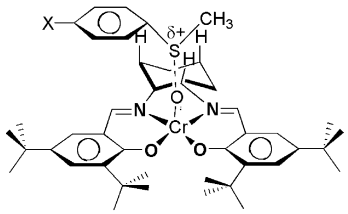
	IIa		IIg		IIh		IIi		IIj	
X	reaction time (min)	% sulfoxide	reaction time (min)	% sulfoxide	reaction time (min)	% sulfoxide	reaction time (min)	% sulfoxide	reaction time (min)	% sulfoxide
H	240	96	150	99	180	82	180	95	300	96
OMe	60	95	25	99	150	92	135	99	180	100
Me	75	93	25	90	160	88	135	87	240	98
F	200	78	120	70	180	65	150	65	300	72
Cl	240	60	150	55	240	68	180	53	320	49
Br	240	61	150	57	240	55	180	50	350	52
$COCH_3$	240	40	150	42	300	59	180	42	380	61
COOH	240	30	150	27	300	51	180	30	380	45

SCHEME 1



stantial steric effect support the mechanism proposed earlier for the oxo(salen)chromium (V) oxidation of organic sulfides, and the mechanism is shown in Scheme 1.

Thus the reaction proceeds through an electrophilic attack of the oxygen of the oxidant at the electron-rich sulfur center of the substrate, and the transition state may be represented as shown below for the reaction of oxo(salen)chromium(V) complex **IIj**.



The negative ρ value for the substituent variation in ArSMe and the positive ρ value for the substituent variation on the salen ligand point out the extent of charge development on the substrate and oxidant in the transition state.

Oxidation of Organic Sulfoxides. Though organic sulfoxides behave similarly to organic sulfides in many oxidation reactions,[35−38] organic sulfoxides are biphilic substrates and they may act as electrophiles as well as nucleophiles, depending on the nature of the oxidant.[39−42] The ability of sulfoxides to trap nucleophilic peroxidic species has been utilized in the design and use of thianthrene 5-oxide as a mechanistic probe in many oxygen atom transfer reactions and for assessing the electrophilic character of oxygen-transfer agents.[41,43,44] It is interesting to recall that organic sulfides act as nucleophiles and sulfoxides as electrophiles toward permanganate ion.[40,45] Another interesting feature of sulfoxide is that it can transfer oxygen atom to the metal ion to produce oxometal species, which in turn can transfer oxygen atom to other substrates[46,47] In the present study, we have observed that the addition of DMSO and MPSO to Cr(III)−salen leads to the formation of a sharp peak at 395 nm similar to pyridine *N*-oxide, indicating the binding of sulfoxide to Cr(III)−salen complex.[29] To understand the behavior of sulfoxides toward oxo(salen)chromium(V) complexes, we have studied the reaction of five oxo(salen)chromium(V) complexes with six aryl methyl sulfoxides. The shift in λ_{max} of **IIa** with the addition of MPSO prompted us to record the absorption spectra of other oxo(salen)chromium(V) complexes, and the λ_{max} values in the absence and presence of MPSO are collected in Table 1. Similar spectral changes have also been observed when DMSO is added to all Cr(V) complexes, and the λ_{max} values in the presence of DMSO are collected in Table 1. With an increase in the concentration of MPSO, the absorbance (OD) of Cr(V) complex goes on increasing, and it attains the maximum OD at [MPSO] 0.1 M. The change in absor-

(35) (a) Thenraja, D.; Subramaniam, P.; Srinivasan, C. *Tetrahedron* **2002**, *58*, 4283. (b) Suthakaran, R.; Rajagopal, S.; Srinivasan, C. *Tetrahedron* **2001**, *57*, 1369.

(36) (a) Srinivasan, C.; Chellamani, A.; Rajagopal, S. *J. Org. Chem.* **1985**, *50*, 1201. (b) Balaiah, V.; Satyanarayana, P. V. V. *Indian J. Chem.* **1978**, *16A*, 966. (c) Srinivasan, C.; Venkatasamy, R.; Rajagopal, S. *Indian J. Chem.* **1981**, *20A*, 505.

(37) (a) Srinivasan, C.; Rajagopal, S.; Chellamani, A. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1839. (b) Manohar, T. C. Ph.D. Thesis, Madurai Kamaraj University, 1991.

(38) (a) Balakumar, S.; Thanasekaran, P.; Rajagopal, S.; Ramaraj, R. *Tetrahedron* **1995**. (b) Adaikalasamy, J. K.; Venkataramanan, N. S.; Rajagopal, S. *Tetrahedron* **2003**, *59*, 3613.

(39) Lahti, D. W.; Espenson, J. H. *Inorg. Chem.* **1999**, *38*, 5230.

(40) (a) Banaerji, K. K. *Tetrahedron* **1988**, *44*, 2929. (b) Rajagopal, S.; Sivasubramaniam, G.; Suthakaran, R.; Srinivasan, C. *Proc. Indian Acad. Sci. (Chem. Sci.)* **1991**, *103*, 637.

(41) (a) Sawaki, Y.; Ogata, Y. *J. Am. Chem. Soc.* **1981**, *103*, 5947. (b) Ballistreri, F. P.; Tomaselli, G. A.; Toscano, R. M.; Conte, V.; Difuria, F. *J. Am. Chem. Soc.* **1991**, *113*, 6209.

(42) (a) Bortolini, O.; DiFuria, F.; Modena, G.; Scadellato, C.; Serimin, P.; *J. Mol. Cat.* **1981**, *11*, 107. (b) Bortolini, O.; Difuria, F.; Modena, G. *J. Mol. Cat.* **1982**, *14*, 53. (c) Campstrini, S.; Conte, V.; DiFuria, F.; Modena, G.; Bortolini, O. *J. Org. Chem.* **1988**, *53*, 5721. (d) Licini, G.; Bonchio, M.; Modenq, G.; Nugent, W. A. *Pure Appl. Chem.* **1999**, *71*, 463. (e) Bonchio, M.; Bortolini, O.; Licini, G.; Moro, S.; Nugent, W. A. *Eur. J. Org. Chem.* **2003**, 507.

(43) (a) Adam, W.; Haas, W.; Sieker, G. *J. Am. Chem. Soc.* **1984**, *106*, 5020. (b) Adam, W.; Haas, W.; Lohray, B. B. *J. Am. Chem. Soc.* **1991**, *113*, 6202. (c) Adam, W.; Golsch, D.; Corth, F. C. *Chem. Eur. J.* **1996**, *2*, 255.

(44) (a) Adam, W.; Golsch, D. *J. Org. Chem.* **1997**, *62*, 115. (b) Deubel, D. V. *J. Org. Chem.* **2001**, *66*, 2696.

(45) (a) Lee, D. G.; Chen, T. *J. Org. Chem.* **1991**, *56*, 5346. (b) Xie, N.; Binstead, R. A.; Clock, E.; Chandler, W. D.; Lee, D. G.; Meyer, T. J.; Thiruvazhi, M. *J. Org. Chem.* **2000**, *65*, 1008.

(46) Arias, J.; Newlands, C. R.; Abu-Omar, M. M. *Inorg. Chem.* **2001**, *40*, 2185.

(47) Arterburn, J. B.; Nelson, S. L. *J. Org. Chem.* **1996**, *61*, 2260.

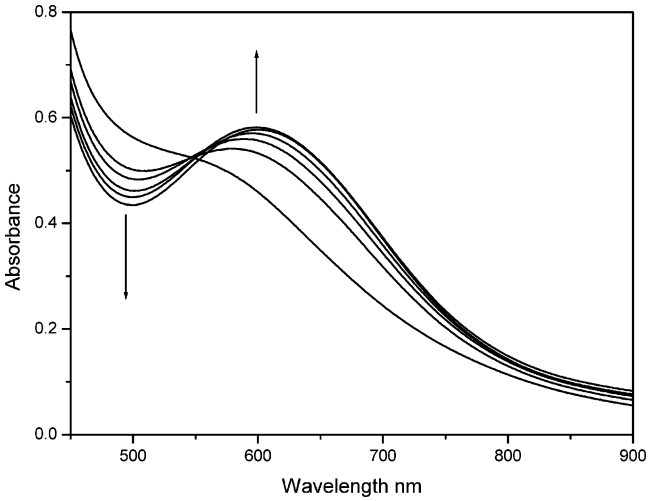


FIGURE 4. Absorption spectra of **IIa** in the absence of MPSO and at 0.025, 0.05, 0.075, 0.1, and 0.125 M MPSO.

bance of Cr(V) complex with the increase in the [MPSO] is shown in Figure 4.

The substantial shift in the λ_{max} and increase in the OD of oxo(salen)chromium(V) ion with [sulfoxide] point out that sulfoxide binds with Cr(V) complexes efficiently and the binding to the metal occurs *via* the oxygen atom of sulfoxide. This behavior of sulfoxide differs from that of organic sulfide toward oxo(salen)chromium(V) ion, and the behavior of oxo(salen)chromium(V) ion differs from that oxo(salen)manganese(V) toward sulfoxides. In the present study, the increase in OD with sulfoxide concentration has been utilized to estimate the binding constant of sulfoxide with oxo(salen)chromium (V) ion. The values of binding constant of MPSO with oxo(salen)chromium-(V) complexes are collected in Table 1 (the details of the estimation of the binding constant are given in the Experimental Section). It is interesting to see that binding constant values are higher with Cr(V) complexes containing 5-Cl salen and 5-Br salen, as expected. Kochi et al.[29] have reported the binding constant of oxo(salen)-chromium(V) ion with DMSO as 7 M^{-1}. When we recorded the absorption spectrum of the oxidant in the presence of sulfoxide at different time intervals, we realized that the oxygenation reaction takes place after the binding of substrate to the oxidant, and the spectral changes are shown in Figure 5.

It is important to point out that we could follow the kinetics of the reaction only if [sulfoxide] > 0.1 M. It has already been indicated that the OD for the Cr(V) ion−sulfoxide adduct reached its maximum when [sulfoxide] is 0.1 M. Thus, all kinetic studies have been carried out by taking [sulfoxide] > 0.1 M. We have followed the oxygenation of organic sulfoxides by measuring the decrease in OD with time at the wavelength collected in Table 1. The linear log OD vs time plot shows that the oxo(salen)chromium(V) ion oxygenation of organic sulfoxides is also first-order with respect to the oxidant. A first-order dependence on the sulfoxide is evident from the plot of k_1 vs [sulfoxide], which is linear (Figure 6). Thus the reaction is total second-order first-order each in the oxidant and in the substrate.

The kinetics of oxygenation of organic sulfoxide by **IIc** was also studied by an EPR technique. The EPR spectra

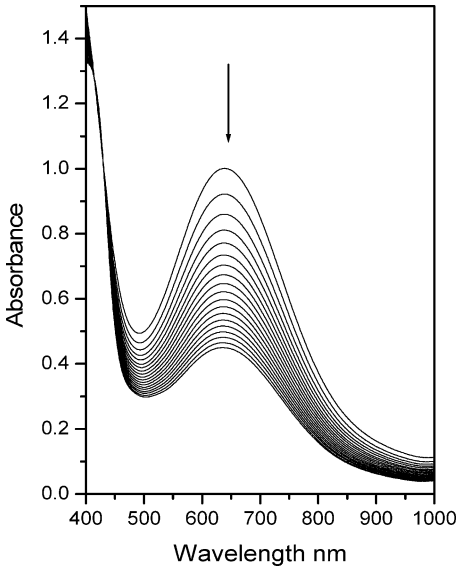


FIGURE 5. Sample run showing the change in OD of **IIc** with time in the presence MPSO.

of the reaction mixture at various time intervals are shown as Figure S3. The concentration of Cr(V) complex was kept at 5×10^{-4} M and that of MPSO at 0.2 M. The calculated g values (1.987 for $[(salen)Cr^{V}{=}O]^{+}$ and 1.983 for Cr(V)−sulfoxide adduct) are found to be in close agreement with the earlier report.[29] From the decrease in the intensity of the Cr(V) signal with time, the rate constant for the reaction with organic sulfoxide was estimated and found to be in close agreement with the results obtained by the spectrophotometric method.

Substituent Effects. The oxygenation reaction of organic sulfoxides is also highly sensitive to the change of substituent in the aryl moiety of aryl methyl sulfoxides [ArS(O)Me] and 5- and 5′-positions of salen in the oxidant (Table 4).

The electron-donating substituents in the aryl ring of ArS(O)Me accelerate the rate, and the electron-withdrawing groups have the opposite effect. To understand the extent of charge separation in the transition state, the k_2 values collected in Table 4 are analyzed using the Hammett equation. The correlation of log k_2 values of ArS(O)Me with Hammett substituent constant values (σ) is good (Figure 7) and the reaction constant values (ρ) are in the range from −1.2 to −1.8 for different oxo-(salen)chromium(V) complexes.

The ρ value for the reaction of sulfoxides with each oxo-(salen)chromium(V) complex is given at the bottom of Table 4. The correlation is not improved if Brown−Okamoto values (σ^{+}) are used instead of σ. The effect of introducing substituents in the salen ligand of the oxidant on the rate of the reaction is also analyzed in terms of the Hammett equation (Supporting Information, Figure S4) and the ρ value is positive ($\rho = 1.1$ for the parent sulfoxide MPSO). The comparison of ρ values observed with oxo(salen)chromium(V) complexes with those of the corresponding Mn and Fe complexes for the oxygenation of organic sulfoxides shows that Cr complexes are more sensitive to the electronic effects.[31b,48]

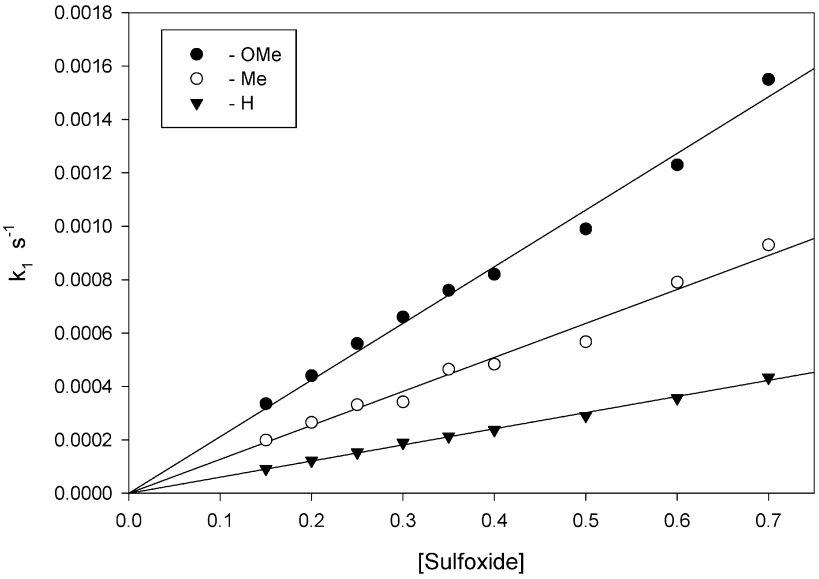


FIGURE 6. Plot of k_1 vs [sulfoxide] for the oxidation of *p*-$XC_6H_4S(O)Me$ with **IIc**.

TABLE 4. Second-Order Rate Constant, k_2, for Oxidation of *p*-$XC_6H_4S(O)Me$ with Oxo(salen)chromium(V) Complexes IIa, IIb, IIc, IId, and IIh in CH_3CN at 298 K

	$k_2 \times 10^4$ M^{-1} s^{-1}					
X	**IIa**	**IIb**	**IIc**	**IId**	ρ (r)	**IIh**
H	1.40 ± 0.02	0.910 ± 0.010	6.30 ± 0.07	7.41 ± 0.12	1.1 (0.990)	1.59 ± 0.04
OMe	3.80 ± 0.08	4.51 ± 0.09	22.0 ± 0.12	24.3 ± 1.4	1.0 (0.930)	4.74 ± 0.09
Me	2.75 ± 0.05	3.82 ± 0.05	13.3 ± 0.02	15.8 ± 0.98	0.9 (0.890)	3.21 ± 0.05
F	0.921 ± 0.020	0.720 ± 0.030	4.70 ± 0.07	5.27 ± 0.33	1.1 (0.977)	1.02 ± 0.03
Cl	0.755 ± 0.010	0.510 ± 0.020	3.21 ± 0.05	4.71 ± 0.24	1.1 (0.986)	0.93 ± 0.02
$COCH_3$	0.520 ± 0.000	0.440 ± 0.010	2.06 ± 0.04	3.10 ± 0.09	1.0 (0.969)	0.52 ± 0.21
ρ	−1.2	−1.8	−1.5	−1.3		−1.4
R	0.984	0.978	0.983	0.971		0.986

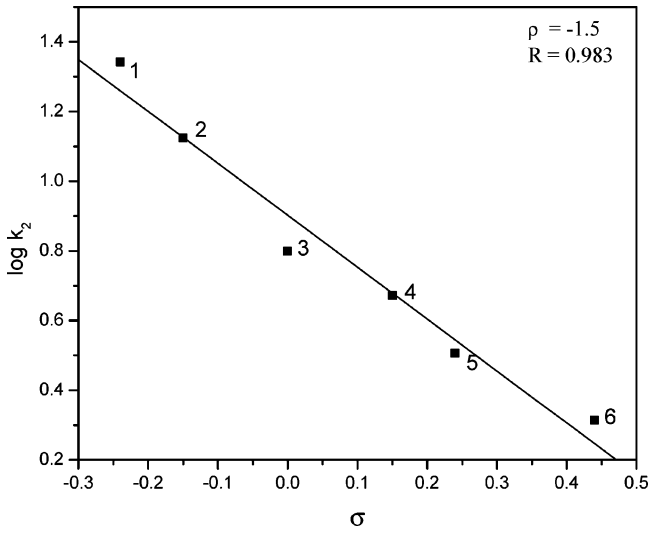
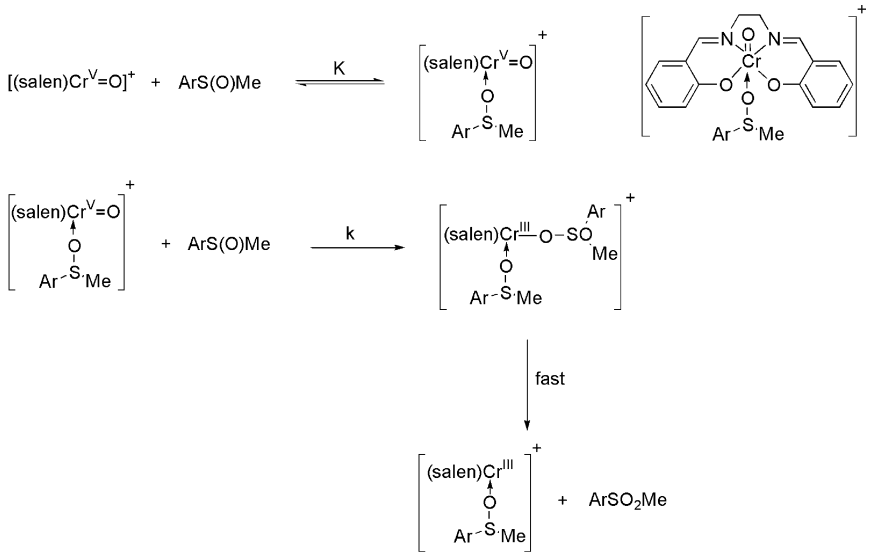


FIGURE 7. Hammett plot for the oxidation of *p*-$XC_6H_4S(O)$-Me with **IIc**: 1, *p*-OMe; 2, *p*-Me; 3, H; 4, *p*-F; 5, *p*-Cl; 6, *p*-$COCH_3$.

Mechanism of Oxidation of Sulfoxides. Though both organic sulfides and sulfoxides behave as nucleophilies toward oxo(salen)chromium(V) complexes, the kinetic aspects seem to be entirely different. This is in striking contrast to the behavior of these substrates toward oxo(salen)iron and oxo(salen)manganese complexes. With oxo(salen)manganese complexes, both substrates have comparable reactivity, and the ρ value is always high with sulfoxides. These observations are accounted for in terms of the bimolecular electrophilic attack of the oxygen of the oxidant at the sulfur center of the substrate having an early transition state for sulfides and a late transition state for sulfoxides. On the other hand, both these substrates follow Michaelis−Menten-type kinetics with oxo(salen)iron complexes, and the substrates bind with oxidant before oxygen transfer to the substrates. In the present study, organic sulfoxides bind with the metal center of oxo(salen)chromium(V) complexes efficiently and shift the λ_{max} of the oxidant to the tune of 40 nm and increase the OD of the oxidant substantially. Thus, the first step in the mechanism of the reaction is binding of sulfoxides to the chromium center of the oxidant *via* oxygen, and the binding is strong and the binding constant is in the range of 10−150 M^{-1}. It is important to mention that such a shift in λ_{max} and an increase in OD have not been observed with oxo(salen)iron and oxo(salen)manganese complexes. Gilheany and co-workers[25] have also shown recently that donor ligands such as pyridine *N*-oxide, triphenylphosphine oxide, and DMSO bind with chromium(V) ion, and Cr(V)−ligand oxide adducts catalyze epoxidation of alkenes more efficiently. In the present study, sulfoxide has a dual role. It is acting as a donor ligand as well as the

(48) Chellamani, A.; Kulandaipandi, P.; Rajagopal, S. *J. Org. Chem.* **1999**, *64*, 2232.

SCHEME 2



substrate. Thus, the real oxidant in the present condition is the chromium(V)−sulfoxide adduct, which oxygenates the excess sulfoxide present in the system. Under the present experimental conditions, at least three different modes of oxidation may be envisaged to account for the kinetics of the reaction:[42e] (i) a bimolecular electrophilic oxygen atom transfer from the free oxo(salen)chromium(V) ion to the sulfoxide, (ii) an inner-sphere nucleophilic oxygen transfer (ligand coupling) proceeding in the oxidant−sulfoxide adduct, and (iii) a bimolecular (outer-sphere) electrophilic oxidation performed by oxidant−sulfoxide adduct at nonligated sulfoxide. In the present study, mechanism (i) is of little importance, as most the oxidant is in the form of oxidant−substrate adduct and it is more reactive compared to the free oxidant. The ligand coupling mechanism (ii) is not favorable, as the oxygen atom of the oxidant and bound sulfoxide are in the trans position (cf. structure 1). Thus, the most probable mechanism is (iii). Hence, the observed spectral and kinetic results can be accounted for in terms of the mechanism shown in Scheme 2.

The strong binding of sulfoxide to the Cr center weakens the Cr═O bond in the oxo(salen)chromium ion, facilitating the oxygen transfer from the oxidant to the substrate. Thus, the kinetic data observed and the reaction constant (ρ) values calculated from the kinetic data are applicable to the catalyzed reaction.

Comparison of Oxo(salen)metal(V) Complexes' Oxidation of Organic Sulfides and Sulfoxides. To get a clear picture of the electrophilicity of the oxo(salen)-metal complexes and the reactivity of these complexes toward biologically important substrates, organic sulfides and sulfoxides, we have used three metal ions, Fe, Mn and Cr. Of these three metal ions, Cr has a special role because of its established utility in synthesis and its carcinogenicity.[11−22] If the reaction between Cr and organic substrates proceeds through an electron-transfer mechanism, radicals will be produced as intermediates, and the redox system is prone to greater toxicity. From the preliminary study of the previous report[28] and by the more extensive present study, we have shown that oxo(salen)chromium(V) complexes oxidize organic sulfides

TABLE 5. Oxidation X−$C_6H_4SCH_3$ with IIa in the Presence of MPSO, PyO, and Ph_3PO

	$k_2 \times 10^3$ M^{-1} s^{-1}			
X	without donor ligand	with MPSO	with PyO	with Ph_3PO
H	1.31 ± 0.03	9.53 ± 0.07	37.3 ± 0.09	48.8 ± 0.08
p-OMe	25.9 ± 0.59	27.8 ± 0.82	90.9 ± 1.21	133 ± 1.3
p-Me	11.4 ± 0.23	19.8 ± 0.55	38.5 ± 0.89	105 ± 1.1
p-F	1.58 ± 0.08	7.51 ± 0.06	17.2 ± 0.24	27.4 ± 0.7
p-Cl	0.93 ± 0.01	5.33 ± 0.05	10.4 ± 0.12	18.5 ± 0.2
p-Br	0.93 ± 0.01	5.10 ± 0.02	9.77 ± 0.09	18.1 ± 0.1
p-CO_2H	0.24 ± 0.02	2.56 ± 0.01	4.68 ± 0.06	7.33 ± 0.07
p-$COCH_3$	0.16 ± 0.01	2.24 ± 0.01	4.69 ± 0.05	7.21 ± 0.05
ρ	−2.8	−1.5	−1.7	−1.8
r	0.965	0.991	0.989	0.994

selectively and the reaction proceeds through a clean bimolecular electrophilic oxidation reaction. Further, the results observed in the present study show that organic sulfoxides have a dual role. When they are used as substrates toward oxo(salen)chromium(V) complexes, the sulfoxide binds with chromium(V) and thus acts as a donor ligand. Thus chromium(V)−sulfoxide complex has the capability to act as a catalyst for the oxidation of organic substrates. To check the catalytic role of organic sulfoxides, the kinetics of the reaction between oxo(salen)chromium(V) complexes and organic sulfides in the presence of MPSO has also been followed, and the data are collected in Table 5 (details are reported separately). These data show that organic sulfoxide acts as a catalyst for the oxidation of organic sulfides. This catalytic activity of sulfoxides is similar to the role of PyO and Ph_3PO, and data obtained in the presence of PyO and Ph_3PO are also included in Table 5.

However, in the case of Mn and Fe complexes, sulfoxides act only as substrates. Thus, the interesting results observed in the present study show the dual role of sulfoxide as substrate and catalyst. It is worthwhile to recall that the electronic nature of the sulfoxide and its interaction with the metal atom play a key role in the global stereoselectivity of the sulfoxidation process. It is known that the overoxidation of sulfoxide to sulfone is

pivotal in enhancing the enantiomeric excess of the sulfoxide by kinetic resolution.[42e] We will address this issue in our future study. The data given in Table 5 show that all donor ligands catalyze the Cr(V) oxidation of organic sulfides and the reaction constant (ρ) obtained with the catalyzed reaction is always small compared to the uncatalyzed oxidation. To get a clearer picture requires further detailed study with several donor ligands and more Cr(V)−salen complexes, which is under progress.

Experimental Section

The ligands salen, 5-Me(salen), 5-Br(salen), 5-Cl(salen), 3,5-di-*tert*-butyl(salen), salophen, salprn, 7,7′-dimethylsalen, cyclo(salen), and 3,5-di-*tert*-butylcyclo(salen) (for an explanation of the abbreviations, cf. Chart 1) were characterized by NMR (details are not given) and Cr^{III} complexes of these ligands were synthesized using established procedures.[25,29−31,49] Iodosylbenzene was prepared by alkaline hydrolysis of iodosobenzene diacetate according to the reported method.[50] The oxo(salen)-chromioum(V) complexes (**caution−Cr(V) compounds are known carcinogens**) **IIa**−**IIj** were obtained from chromium-(III) complexes **Ia**−**Ij** by the general procedure described below: A slight excess of iodosylbenzene is added to Cr^{III}−salen complex dissolved in ∼25 mL of CH_3CN. The color of the reaction mixture turned from orange to dark green. This slurry is stirred for 20 min and then filtered to remove the unreacted iodosylbenzene. Ether is slowly added to the dark filtrate in order to precipitate crystals of oxo(salen)chromium-(V) salts. The purity of Cr(III) and Cr(V) complexes was checked by IR, UV−vis, EPR, and ESI-MS methods.[25−29](ESI-MS results of **Ib** and **IIb** are shown in the Supporting Information, Figure S5, and EPR spectra of **Ie** and **IIe** are also given in the Supporting Information, Figure S6). The aryl methyl sulfides and sulfoxides were obtained from known synthetic methods[28,48,51] and their purity checked by GC. All other reagents were of AnalaR grade or used after purification. The kinetic study of the reaction was performed after confirming the purity of the reactants and solvents used in this system.

Kinetic Measurements. The spectra of Cr(III) and oxochromium(V) complexes used in the present study and the kinetics of oxygen atom transfer from oxochromium(V) complexes to organic sulfides and sulfoxides were followed by diode array spectrophotometer. The kinetic studies for the oxygenation of organic sulfides and sulfoxides were carried out in CH_3CN under pseudo-first-order conditions with a substrate:oxidant ratio of at least 10:1. The progress of the reaction was monitored by following the decay of absorbance of oxochromium(V) ion at definite time intervals at the wavelengths collected in Table 1.

Electron Paramagnetic Resonance Studies. The EPR spectra of the Cr(III) and Cr(V) complexes were recorded at 77 K and room temperature, respectively, in CH_3CN. For the kinetic study, the spectra were acquired at a frequency of ca. 1.39 GHz with a field at 335 ± 40 mT and at constant modulation amplitude.

Electrochemical Studies. The redox potentials of the complexes **IIa**−**IIe** and **IIh**−**IIj** were measured in CH_3CN solution at a glassy carbon working electrode, platinum wire auxiliary electrode, and silver wire quasi-reference electrode, and potentials were corrected to values vs Ag/Ag^+ via an internal standard (Ferrocene) containing 0.1 M tetrabutylammonium percholorate as the supporting electrolyte. The reductive degradation of oxo(salen)chromium(V) ion is also readily apparent by the shape of the CV wave in CH_3CN solution. The large anodic current observed on the reverse scan is symptomatic of electrode pollution. The E_{red} values obtained for oxo-(salen)chromium(V) complexes are collected in Table 1.

Estimation of Binding Constants of Sulfoxides with Chromium(V) Complexes. The complexation/adduct formation of DMSO/MPSO (donor ligand, DL) with the oxo(salen)-chromium(V) cation was monitored by UV−vis spectroscopy. A 5×10^{-4} M solution of oxo(salen)chromium(V) ion in acetonitrile, taken in a quartz cuvette with 1 cm path length, was treated with successive aliquots of a concentrated solution of the donor ligands in the same solvent. The absorption spectrum of the oxo(salen)chromium(V) ion exhibited a red shift upon the addition of donor ligands. The formation of complex/adduct was evident from the color change (dark green to emerald green). By measuring the OD at different concentration of a particular donor ligand at the appropriate λ_{max}, the binding constants are calculated by using the modified Benesi−Hildebrand (double-reciprocal plot) equation.[52]

$$\frac{[\text{oxidant}][\text{donor ligand}]}{\Delta OD} = \frac{[\text{oxidant}] + [\text{donor ligand}]}{\Delta\epsilon} + \frac{1}{K_f \Delta\epsilon}$$

In the above equation, ΔOD and $\Delta\epsilon$ are the difference in the absorption intensities and molar extinction coefficients of $[O{=}Cr^{V}(salen)]^+$ in the presence and absence of donor ligand, respectively, and K_f is the equilibrium constant for the formation of adduct or complex. The plot of [oxidant][donor ligand]/ΔOD vs [oxidant] + [donor ligand] is linear, and from the values of slope and intercept, K_f values for the complex formation with donor ligands have been calculated and given in the Table 1.

Stoichiometry and Product Analysis. The stoichiometry of the reaction between $[O{=}Cr^{V}(salen)]^+ClO_4$ complex and sulfides/sulfoxides was studied by taking different ratios of [oxidant] and [substrate]. After the reaction is over, the concentration of excess oxidant was estimated from the change in OD and the molar extinction coefficient (ϵ). From the measurement of change in concentration it was found that the oxidant and the substrates react in a ratio of 1:1 and the overall reaction may be represented by eq 1.

$$[O{=}Cr^{V}(salen)]^+ + \text{ArSMe/ArS(O)Me} \rightarrow [Cr^{III}(salen)]^+ + \text{ArS(O)Me/ArSO}_2\text{Me} \quad (1)$$

In a typical experiment, 0.2 mM of substrate (ArSMe) was added to a 0.2 mM solution of oxochromium(V) complex in 5 mL of solvent (CH_3CN). The solution was stirred at 298 K for 1−6 h, depending upon the nature of substrate and oxidant (vide infra). After the removal of the solvent under reduced pressure, the organic product was extracted with ether and dried, and the solvent was removed. Then the resulting residue was analyzed by GC and IR. The IR spectrum of the product was found to be identical with that of sulfoxide (ArS(O)Me), having its S=O stretching frequency in the characteristic region 1070−1030 cm^{-1} when organic sulfides were taken as substrates. The GC analysis of the product also indicated that the formation of sulfoxide as the only product under the present experimental conditions. The absorption spectrum of the inorganic product of the reaction was similar to that of Cr^{III}−salen complex, confirming the formation of sulfoxide and Cr^{III}−salen as the products. When organic sulfoxide was used as the substrate, the corresponding sulfone was formed as the product.

(49) (a) Joly, G. D.; Jacobsen, E. N. *Org. Lett.* **2002**, *10*, 1796. (b) Martinez, L. E.; Leighton, J. L.; Casten, D. H.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995**, *117*, 5897. (c) Larrow, J. F.; Jacobsen, E. N.; Gao, Y.; Hong, Y.; Nie, X.; Zepp, C. M. *J. Org. Chem.* **1994**, *59*, 1939.

(50) Saltzman, H.; Sharefkin, J. G. *Organic Synthesis*; Weley: New York, 1973; Collect Vol. V., p 658.

(51) Bordwell, F. G.; Andersen, H. M. *J. Am. Chem. Soc.* **1953**, *75*, 6021.

(52) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703. (b) Person, W. B. *J. Am. Chem. Soc.* **1965**, *87*, 167.

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Supporting Information Available: Hammett plot of E_{red} values of complexes **IIa**−**IIe** vs 2σ, spectra showing the change in OD of **IIc** for its reaction with MPS, EPR spectra of Cr(V)−salen complex and the change in the intensity for the reaction of **IIC** with MPSO, Hammett plot for the oxidation of $C_6H_5S(O)Me$ by **IIa**−**IId**, ESI-MS spectra for **Ib** and **IIb**, and EPR spectra of **Ie** and **IIe**. This material is available free of charge via the Internet at http://pubs.acs.org.

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