Mechanism of Selective Oxidation of Organic Sulfides with Oxo(salen)chromium(V) Complexes

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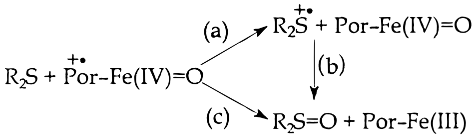
The selective oxidation of organic sulfides to sulfoxides by oxo(salen)chromium(V) complexes in acetonitrile is overall second-order, first-order each in the oxidant and the substrate. The rate constant, k_2, values of several para-substituted phenyl methyl sulfides correlate linearly with Hammett σ constants and the ρ values are in the range of −1.3 to −2.7 with different substituted oxo(salen)chromium(V) complexes. The reactivity of different alkyl sulfides is in accordance with Taft's steric substituent constant, E_S. A mechanism involving direct oxygen atom transfer from the oxidant to the substrate rather than electron transfer is envisaged. Correlation analyses show the presence of an inverse relationship between reactivity and selectivity in the reaction of various sulfides with a given oxo(salen)chromium(V) complex and vice versa. Mathematical treatment of the results shows that this redox system falls under strong reactivity−selectivity principle (RSP).

Introduction

To mimic active intermediates in enzyme-catalyzed oxidation reactions, metalloporphyrin and metallosalen complexes [salen = N,N'-bis(salicylidine)ethylenediaminato)] of iron, manganese, chromium, and ruthenium have been used as model compounds and have been shown to be capable of catalyzing oxygen atom transfer from monooxygen sources such as iodosylbenzene, H_2O_2, peracids, hypochlorite, etc. to saturated and unsaturated hydrocarbons and other organic substrates.[1−14] Although participation of discrete, high-valent oxometal intermediates in the oxidation of organic substrates by heme proteins and related model systems is widely accepted, unambiguous assignment of the electronic configuration of the metal center in these intermediates has presented a difficult challenge. Despite the synthetic versatility of these systems, controversy exists on the mechanistic details of these oxygen atom transfer reactions.[10,11] It has been proposed that the sulfoxidation of sulfides by hemoproteins is initiated by one electron transfer from the sulfide to the iron(IV) oxoporphyrin radical cation[15a] ($Por^{\bullet+}$-Fe(IV)═O), which is suggested to be the active species in these reactions (Scheme 1)

Scheme 1



As illustrated in Scheme 1 (paths a and b), the sulfoxide is then formed by reaction of the radical cation with Por-Fe(IV)═O (oxygen rebound). Recently, Baciocchi et al.[15b] found clear evidence for the formation of sulfide radical cation in the oxidation of sulfides by horseradish peroxidase. On the other hand, the mechanism appears to be less defined for the cytochrome P-450 oxidation of organic sulfides. Though an electron-transfer mechanism is possible, a direct oxygen transfer from the iron oxoporphyrin radical cation to the substrate is also a viable mechanism as shown in Scheme 1, path c. Thus, the

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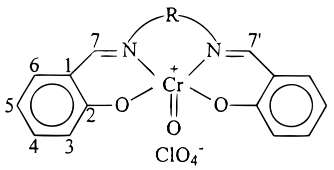

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R =

1a. – CH_2CH_2 –

1b. – $CH_2CH_2CH_2$ –

1c. o – C_6H_4 –

1d. – CH_2CH_2 –; 7, 7' – $(CH_3)_2$

Figure 1.

situation is not clear on the mechanism of oxidation of sulfides with several oxometal ions.

Furthermore, in the oxygentation reactions of some organic substrates catalyzed by metal−salen complexes, the formation of oxometal species is rate determining rather than the oxygen atom transfer step.[10] Thus, it becomes difficult to understand the mechanism of oxygen transfer from oxometal ion to the organic substrate.

Recently, we have proposed single electron transfer from organic sulfide to the oxometal complex as the rate-controlling step in the oxygen atom transfer reaction from several cationic oxo(salen)manganese(V) and oxo(salen)-ruthenium(V) complexes to sulfides.[13,14] A major disadvantage of manganese porphyrin and salen complexes is that manganese complexes catalyzed oxidation reactions display considerable radical character leading to radical byproducts and losses in selectivities due to the formation of radicaloid intermediates. Kochi and co-workers have concluded that the epoxidation of alkenes with oxomanganese(V) complexes favored a radical pathway, whereas oxochromium(V) favored the S_N2 mechanism.[6,7] To learn the mechanism and synthetic utility, the oxidation of organic sulfides to sulfoxides with four oxo(salen)chromium(V) $[O{=}Cr^V(salen)]^+$ complexes (Figure 1) has been studied and the results are discussed in this paper.

Results and Discussion

In the present study, $[O{=}Cr^V(salen)]^+$ complexes **1a**−**d** have been prepared from Cr^{III}−salen complexes and iodosylbenzene and then used for the oxidation of organic sulfides (eq 1)

$$[Cr^{III}(salen)]^+ + PhIO \rightarrow [O{=}Cr^V(salen)]^+ + PhI \quad (1)$$

The formation of oxometal complexes is confirmed by their absorption spectra, which are similar to the previous reports.[6,8,16] The kinetics of oxidation of several aryl methyl and dialkyl sulfides with $[O{=}Cr^V(salen)]^+$ complexes have been studied in acetonitrile by spectrophotometric techniques (details are given in the Experimental Section). The rate of PhIO oxidation of these organic sulfides has been checked and found to be very slow under the present experimental conditions. Similar observations have been reported previously by us and also by others.[17,18]

The oxidation reaction is overall second-order, first-order with respect to the oxidant and the substrate. The first-order in $[O{=}Cr^V(salen)]^+$ is evident from the linear log o.d. vs time plots and in the substrate from the linear k_1 vs [sulfide] plots shown in Figure 2 for different sulfides. To understand the effect of acid on the kinetics of this reaction, the rates at different concentrations of trichloroacetic acid were measured, and the data are collected in Table 1. The k_1 value increases with increase in [acid], confirming the catalytic role of acid in this reaction. The addition of acid shifts the λ_{max} of $[O{=}Cr^V(salen)]^+$ from 560 to 570 nm, pointing out that carboxylate group may be coordinated to the metal thereby enhancing the reactivity of the oxidant. We have observed that addition of ligands such as imidazoles, pyridine, heteroaromatic oxides such as pyridine *N*-oxide, triphenylphosphine oxide, etc. to the $[O{=}Cr^V(salen)]^+$ and sulfide system enhances the rate, and in all these cases the ligands are coordinated to the metal (the details will be reported separately). Therefore, at this stage we conclude that the catalytic activity of trichloroacetic acid is due to the coordination of carboxylate ion to the metal.

Kinetic studies in different ratios of solvent systems (acetonitrile−H_2O; Table 1) revealed that the rate of oxidation is facilitated with the increase in water content, indicating charge separation in the transition state. Since the influence of solvent on the rate is very large, this increase may be due not only to a change in polarity but also due to other effects. We have observed that the addition of H_2O shifts λ_{max} of $[O{=}Cr^V(salen)]^+$ from 560 to 600 nm. This leads us to believe that H_2O is coordinated to the metal (like triphenylphosphine oxide) and the H_2O coordinated oxidant enhances the rate to a larger extent. H_2O is likely to act as the axial ligand.

Substituent Effects. The data provided in Table 2 point out that the redox reaction between $[O{=}Cr^V(salen)]^+$ and organic sulfides is highly sensitive to the nature of the substrate and the structure of the ligand of Cr^V complex. The reactivity is in the order dialkyl sulfides > aryl methyl sulfides. The introduction of substituents in the para position of the phenyl ring of PhSMe alters the rate appreciably, i.e., the electron-releasing substituents accelerate the rate and the electron-withdrawing groups decelerate it. The kinetic data have been analyzed with the Hammett equation, and the plot of log k_2 vs Hammett σ constants is linear in all four complexes **1a**−**d**, giving the ρ values -2.68 ($r = 0.973$), -1.14 ($r = 0.970$), -2.15 ($r = 0.989$), and -2.02 ($r = 0.987$),respectively, at 298 K (a representative plot is shown in Figure 3). The correlation is not improved if σ^+/σ^- values are used instead of Hammett's σ constants. Substantial change in the ρ value is observed with the change of structure of the Cr^V complex. If we compare the reactivity of four Cr complexes with the ρ values (selectivity), a reverse trend is noticed between the reactivity and selectivity; i.e., this redox system is in accordance with the reactivity−selectivity principle (RSP). We have also observed recently the operation of RSP in

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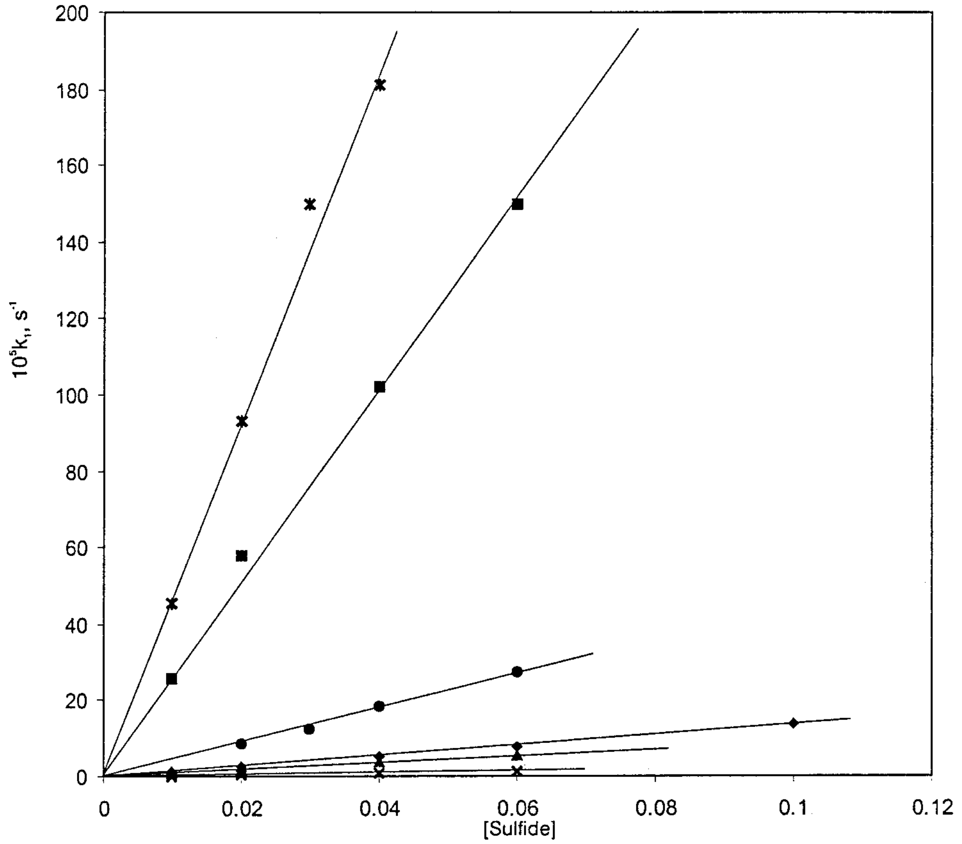

Figure 2. Plots of k_1 versus [sulfide] for the oxidation of **1a** with p-XC_6H_4SMe and R_2S: ◆, X = H; ■, X = OMe; ▲, X = Cl; ×, X = $COCH_3$; *, DES; ●, DTBS.

Table 1. Effect of Changing the [Cl_3CCO_2H] and the Solvent Composition on the Rate of Oxidation of Methyl Phenyl Sulfide by 1a at 298 K[a]

[Cl_3CCO_2H], M	10^5k_1,[b] s^{-1}	AN/H_2O	10^5k_1, s^{-1}
	2.62	100	2.62
0.01	8.89	99.2−0.8	6.30
0.02	16.3	90−10	13.4
0.05	22.4	75−25	26.2
0.10	30.7	60−40	29.5
0.20	37.7	50−50	56.5
0.40	70.5		

[a] General conditions: [**1a**] = 0.001 M, [MPS] = 0.02 M. [b] Solvent CH_3CN (AN).

Table 2. Second-Order Rate Constant, k_2, Values for Oxo(salen)Chromium(V) Complexes 1a−d Oxidation of ArSR and R_2S in CH_3CN at 298 K[a,b]

$XC_6H_4SCH_3$, X =	$k_2 \times 10^3$ M^{-1} s^{-1}			
	1a	**1b**	**1c**	**1d**
H	1.31 ± 0.03	29.4 ± 0.51	9.30 ± 0.20	1.13 ± 0.21
p-OMe	25.9 ± 0.03	111 ± 4.0	62 ± 2.9	6.72 ± 0.62
p-Me	11.4 ± 0.23	56.1 ± 0.10	19.9 ± 0.50	2.31 ± 0.25
p-Cl	0.93 ± 0.01	20.5 ± 0.50	3.25 ± 0.11	0.56 ± 0.23
p-Br	0.93 ± 0.01	20.6 ± 0.60	3.33 ± 0.50	0.58 ± 0.25
p-CO_2H	0.24 ± 0.02	13.0 ± 0.40	1.26 ± 0.04	0.17 ± 0.03
p-$COCH_3$	0.16 ± 0.01	12.0 ± 0.10	1.06 ± 0.06	0.13 ± 0.03

	$k_2 \times 10^2 M^{-1}s^{-1}$		
R_2S, R =	**1a**	**1b**	**1c**
Et	4.57 ± 0.11	115 ± 2.12	5.03 ± 0.12
n-Pr	3.55 ± 0.06	54.0 ± 1.21	4.03 ± 0.32
i-Pr	1.35 ± 0.03	31.0 ± 0.51	2.53 ± 0.31
n-Bu	1.63 ± 0.03	32.3 ± 0.14	2.73 ± 0.62
s-Bu	0.87 ± 0.02	10.4 ± 2.21	1.33 ± 0.11
t-Bu	0.22 ± 0.05	4.2 ± 1.01	0.76 ± 0.11

[a] General conditions: $[O{=}Cr^V(salen)]^+ClO_4^-$ = 0.001 M; [substrate] = 0.02 M. [b] The error quoted in k_2 is the 95% confidence limit of student's t test.

the oxo(salen)managanese(V) oxidation of organic sulfides and sulfoxides.[13]

A useful clue on the mechanism of $[O{=}Cr^V(salen)]^+$ oxidation of organic sulfides can be derived by comparing the ρ values observed in the present study with the ρ values obtained on other metal ions oxidation of similar substrates. In the uncatalyzed Cr^{VI} ($HCrO_4^-$) oxidation of aryl methyl sulfides, the ρ value is −1.80 in 50% (v/v) aqueous acetonitrile, and in the picolinic acid catalyzed Cr^{VI} oxidation, the ρ value is −1.07.[19,20] These results led the authors to postulate a single electron transfer from sulfide to Cr^{VI} in the rate-controlling step of uncatalyzed oxidation. On the other hand, two alternate mechanisms viz., one-electron transfer or nucleophilic attack of sulfide on the chromium of Cr^{VI}−picolinic acid complex in the rate-determining step have been proposed in the catalyzed oxidation. Ganesan et al.[21] observed a ρ value of −1.89 in the carboxylato-bound oxochromium(V) oxidation of aryl methyl sulfides. The ρ values of −0.20 and −3.21, respectively, have been observed in the cyto-

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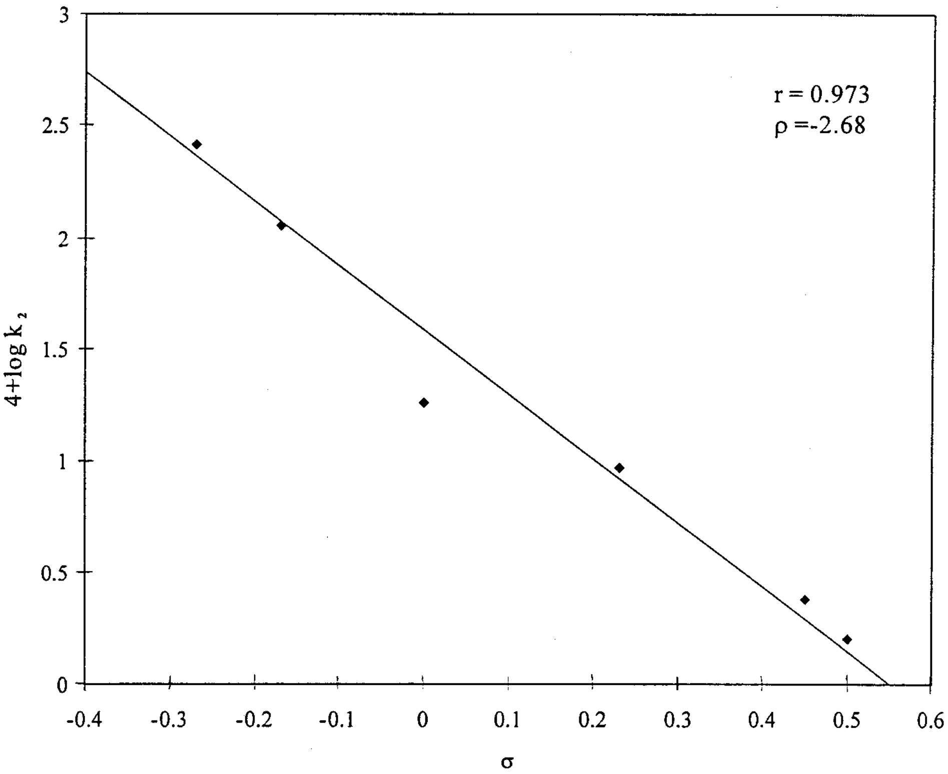

Figure 3. Hammett plot for the oxidation of aryl methyl sulfides by **1a** at 298 K.

chrome P450 and $Fe(NN)_3^{3+}$ (NN = 2,2′-bipyridyl or 1,10-phenanthroline) oxidation of ArSMe.[22,23] Single electron transfer in the rate-controlling step has been postulated in the above oxidation reactions. For the oxidation of thioanisoles by oxo(phosphine)ruthenium(IV) complexes, Takeuchi and co-workers[24] have suggested a single electron-transfer mechanism based on the excellent correlation between log k_x/k_H and σ^- values ($\rho = -1.5$). However, nucleophilic attack of sulfide on the metal center has been postulated in the permanganate ion ($\rho = -1.52$),[25] lead tetraacetate ($\rho = -2.1$),[26] pyridinium halochromates ($\rho = -2.1$),[27] and ruthenate ($\rho = -0.66$)[28] oxidation of ArSMe. These examples show that the magnitude (high or low) of ρ value cannot be taken as evidence in favor of S_N2 or SET mechanism in a particular reaction.

Oxidation of Dialkyl Sulfides. To understand the reactivity of alkyl sulfides toward Cr^V(salen) complexes and the role of steric effect in this reaction, the kinetics of oxidation of several dialkyl sulfides with the Cr^V complexes **1a**−**c** have been studied, and the relevant data are collected in Table 2. The observed kinetic data point out that alkyl sulfides are more reactive than aryl sulfides and the reaction is sensitive to steric effect. To understand the contribution of polar and steric effects on this oxidation, we have analyzed the data in terms of Taft's equations (eqs 2−4)

$$\log k = \log k^0 + \rho^* \sigma^* \quad (2)$$

$$\log k = \log k^0 + \delta E_S \quad (3)$$

$$\log k = \log k^0 + \rho^* \sigma^* + \delta E_S \quad (4)$$

where σ^* and E_S are the polar and steric substituent constants and ρ^* and δ are the corresponding susceptibility constants. Though the correlation of log k with σ^* is not satisfactory, the kinetic data are better correlated with E_S values (eq 3) and the δ values are in the range of 0.6−1.3 for three oxochromium(V) complexes. The use of multiparmeter (eq 4) does not improve the correlation. These arguments point out the predominant role of steric effect over polar effect in this reaction.

Mechanism of $[O{=}Cr^V(salen)]^+$ Oxidation of Organic Sulfides. From the recent literature, it is known that oxygen atom transfer to organic sulfides from oxometal complexes proceeds generally by two different mechanisms. Single electron transfer from the substrate to the oxidant is the rate-determining process for the oxidation of ArSR with peroxy benzoate,[29] hydroperoxidase,[30] Ce^{IV} ,[31] and oxoruthenium(IV)[24] complexes. On the other hand, the oxidation of sulfides by peroxoanions,[32]

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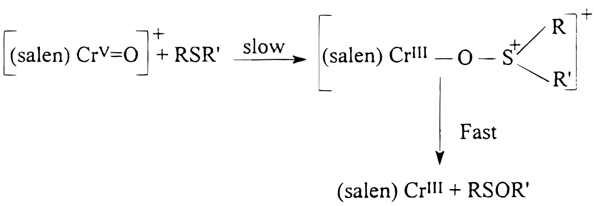
Table 3. Second-Order Rate Constant, k_2, Values at Three Different Temperature, and Values of Enthalpy($\Delta H^{\ddagger}$) and Entropy($\Delta S^{\ddagger}$) of Activation for $[O{=}Cr^{V}(salen)]^{+}PF_6^{-}$ Oxidation of *p*-XC_6H_4SMe in CH_3CN[a]

	$k_2 \times 10^4$ M^{-1} s^{-1}				
X	288 K	298 K	308 K	($\Delta H^{\ddagger}$), kJ mol^{-1}	$-(\Delta S^{\ddagger})$, J K^{-1} mol^{-1}
p-OMe	59.7 ± 2.0	112 ± 4.0	230 ± 7.60	48.1 ± 2.5	120.6 ± 9.2
p-Me	26.1 ± 1.6	41.6 ± 2.5	90.1 ± 4.4	44.4 ± 4.2	141.5 ± 15.1
H	11.7 ± 0.5	20.1 ± 1.0	45.2 ± 2.0	48.6 ± 3.3	132.7 ± 12.1
p-Cl	7.10 ± 0.3	15.3 ± 1.0	32.2 ± 1.8	54.8 ± 4.2	114.7 ± 14.2
p-Br	6.80 ± 0.4	11.6 ± 1.0	23.1 ± 1.7	44.4 ± 5.4	152.4 ± 19.3
p-$COCH_3$	1.02 ± 0.17	2.13 ± 0.1	5.00 ± 0.3	57.8 ± 6.7	121.8 ± 21.2
p-CO_2H	1.42 ± 0.1	3.20 ± 0.1	7.90 ± 0.4	62.4 ± 3.8	102.1 ± 9.2

[a] General conditions: $[O{=}Cr^{V}(salen)]^{+}PF_6^{-} = 0.001$ M; [sulfide] = 0.02 M.

molybdenum peroxypolyoxoanions,[33] sulfamyloxaridines,[34] phenyliodosodiacetate,[35] pyridinium halochromates,[26,36] and permanganate[25] follow S_N2 mechanism. However, a dual mechanism has been proposed in some oxidation reactions.[19]

In the present study, the nucleophilic attack of sulfide on the Cr center may be excluded, as it is difficult to explain the formation of sulfoxide from such a formulation. The coordination of the substrate to the metal is not significant, which is evident from the following experimental observations: (i) when the substrate is added to $[O{=}Cr^{V}(salen)]^{+}$ there is little change in the absorption spectrum of the latter. On the other hand, addition of trichloroacetic acid, H_2O, and ligands such as imidazole and pyridine *N*-oxide to $[O{=}Cr^{V}(salen)]^{+}$ produces a substantial shift in the λ_{max}. These spectral and kinetic observations point out that even if the substrate binds to the oxidant, the binding is weak and equilibrium constant for such binding is small. (ii) The reaction is clearly first order in the substrate, and no saturation kinetics with respect to substrate is observed. If the reaction proceeds through electron transfer in the rate-controlling step, Cr^{IV} would have been formed as the intermediate. During the course of the reaction, we have not observed any spectral evidence for Cr^{IV}. If Cr^{IV} is formed during the reaction, addition of Mn^{II} will influence the rate.[37] When the reaction between $[O{=}Cr^{V}(salen)]^{+}$ and PhSMe was carried out at different concentration of Mn^{II}, no substantial change in the k_1 value was observed. This observation also rules out the formation of Cr^{IV} in the rate-controlling step. The reactivity of similar electron donors is in accordance with their oxidation potentials. Oxidation potentials of diethyl sulfide and methyl phenyl sulfide are 1.65 and 1.53 V, respectively. The higher reactivity of diakyl sulfides compared to aryl methyl sulfides also (Table 2) rules out the operation electron-transfer mechanism. Baciocchi et al.[31] postulated electron-transfer mechanism for Ce^{IV} oxidation of organic sulfides as they observed lower reactivity for dialkyl sulfides. The kinetic and spectral observations led us to conclude that the reaction proceeds through the electrophilic attack of oxygen at the sulfur center of the organic sulfide (eq 5). Furthermore, the values of thermodynamic parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (Table 3) for the reaction of $[O{=}Cr^{V}(salen)]^{+}$-PF_6^{-} with ArSMe are also in favor of the electrophilic attack of oxidant on the substrate.[38]



(5)

As the reaction is being carried out in pure acetonitrile and the rate of reaction is not affected by the presence of oxygen(similar results are observed under inert atmosphere), the origin of oxygen for the product, ArSOMe, is the oxygen in the $O{=}Cr^{V}$ complex.

The Reactivity−Selectivity Principle. Recently, we have observed the operation of the reactivity−selectivity principle (RSP) in the oxidation of organic sulfides and sulfoxides by oxo(salen)manganese(V) complexes.[13] As the four oxo(salen)chromium(V) complexes chosen for the present study show appreciable change in the reactivity and the ρ values (selectivity), it is natural to check the validity of RSP in this redox reaction also. The second-order rate constants for the reaction of several para-substituted phenyl methyl sulfides with each of the oxo(salen)chromium(V) complexes **1a**−**d** are collected in Table 2.

Similar to earlier approaches, we have analyzed the kinetic data using a method advocated by Exner[39] to verify the operation of RSP in the present study. Equations 6 and 7 were used to analyze the data given in Table 2

$$\log k_{F_i} = a + b \log k_{S_i} + \epsilon_i \qquad (6)$$

$$\Delta = (\sum_i \log k_{F_i} - \sum_i \log k_{S_i})/N \qquad (7)$$

In eqs 6 and 7, k_{Fi} and k_{Si} are the second-order rate constants for the reactions of fast and slow reagents (oxo complexes), respectively, with each sulfide, ϵ_i is the error of the log k_{Fi} versus log k_{Si} correlation, and Δ is the mean difference. The values of b and Δ were calculated for all of the five possible combinations of one fast and one slow reagent (among the four oxo complexes) with a series of similar substrates. The results summarized in Table 4 show a valid RSP in all cases as the value of b is less than unity and Δ is not too small.

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Table 4. Results of Correlation between log k_{Fi} and log k_{Si} According to Eq 6 for Aryl Methyl Sulfides

	oxo(salen)chromium(V) complexes (F and S)				
results	**1a** and **1b**	**1d** and **b**	**1a** and **1c**	**1a** and **1d**	**1b** and **1c**
r	0.973	0.973	0.973	0.981	0.993
b	0.465	0.625	0.843	0.730	0.548
Δ	1.11	1.55	0.691	0.285	0.682

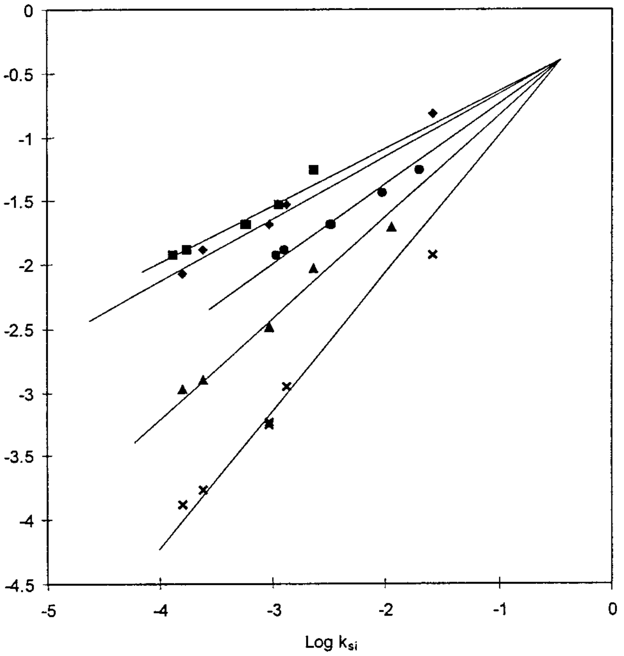

Figure 4. Plot of log k_{Fi} versus with log k_{Si} for the reactions of aryl methyl sulfides with: ◆, **1a** + **1b**; ■, **1d** + **1b**; ▲, **1a** and **1c**; ×, **1a** and **1d**; ●, **1b** and **1c**.

In a reaction series involving more than one reagent and the same set of substrates, the existence of a magic point 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 and the correlations produce one magic point (Figure 4). The magic point is situated on the side of high reactivity, as expected for a strong RSP. It is interesting to point out that two magic points were obtained in the oxo(salen)manganese(V) oxidation of organic sulfides and sulfoxides. The observation that the present reaction series obeys RSP may be taken as evidence for the operation of similar mechanism in all reactions.

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.[40] Though optically active $\mathrm{Mn^V}$–salen complexes have attracted the attention of chemists to use them in the epoxidation of olefins and oxidation of alkyl aryl sulfides, oxidations using other metallosalen complexes as catalysts have not been fully examined. $\mathrm{Mn^V}$–salen complexes prefer radical pathway thus less selective. On the other hand, $\mathrm{Cr^V}$–salen complexes oxidation proceeds by a polar mechanism favoring more selectivity. It is interesting to compare the present results with those observed with $\mathrm{Mn^V}$–salen complexes toward organic sulfides. With the parent oxo(salen)metal complex, the ρ value is −1.86 in $\mathrm{Mn^V}$ and −2.68 with $\mathrm{Cr^V}$. This comparison seems to point out that with $\mathrm{Cr^V}$–salen oxidation of organic sulfides the transition state is more productlike, leading to more selective formation of sulfoxide. This leads to the anticipation of superior enantioselectivity if chiral chromium(V)–salen is chosen as the oxidant because a relatively late transition state suggests a strong interaction of the incoming sulfide with the chiral ligand around the metal. To check the success of selectivity achieved with oxo(salen)chromium(V) complexes, we have studied the synthetic utility of this redox reaction and the details are presented in Table 5. The data given in Table 5 highlight the importance of $\mathrm{Cr^V}$–salen complex for the selective oxidation of sulfide to sulfoxide. The percentage conversion is highly sensitive to the nature of the substituent in the phenyl ring of PhSMe and the structure of Cr(V) complex. The detailed study on the synthetic aspects of this reaction will be reported separately.

Table 5. Selective Oxidation of p-X-C_6H_4-S-CH_3 and R_2S in CH_3CN at 298 K by Ia-C

	1a		**1b**		**1c**	
	reaction time (min)	% of sulfoxide	reaction time (min)	% of sulfoxide	reaction time (min)	% of sulfoxide
X						
H^a	150	52	60	99	180	95
H^b	240	96	150	99		
OMe	60	95	25	99	35	99
Me	75	93	25	90	35	87
Cl	240	60	150	55	180	53
Br	240	61	150	57	180	50
$COCH_3$	240	40	150	42	180	42
CO_2H	240	30	150	27	180	30
R_2S						
Et	45	98	20	99	35	99
Pr	45	83	20	87	35	86
Pr^i	45	68	20	62	35	63
Bu	45	60	20	65	35	65
Bu^s	45	60	20	67	35	69
Bu^t	45	35	20	49	35	47

[a] General conditions: $[\mathrm{O{=}Cr^V(salen)}]^+ \mathrm{ClO_4}$ 0.002 M and [p-X-C_6H_4-S−Me]/[R_2S] 0.002 M. [b] Longer period and other conditions are same as a.

Temperature Dependence. The kinetics of $\mathrm{O{=}Cr^V}$ oxidation of aryl methyl sulfides have been followed in three different temperatures and the values of enthalpy-($\Delta H^{\ddagger}$) and entropy($\Delta S^{\ddagger}$) of activation evaluated from the Eyring equation are collected in Table 3. The $\Delta H^{\ddagger}$ (44–62 kJ $\mathrm{mol^{-1}}$) and $\Delta S^{\ddagger}$ (−152 to −102 J $\mathrm{K^{-1}mol^{-1}}$) values are in favor of two electron transfer rather than single electron transfer in the rate-controlling step of the reaction.[41] The Hammett reaction constant, ρ, values at 288, 298, and 308 K are −2.10, −1.96, and −1.91, respectively, pointing to a decrease in selectivity with an increase in temperature, i.e., with an increase in the reactivity. Thus, the redox reaction obeys the RSP.[39]

Comparison with Carboxylato-Bound Chromium(V) Ion Oxidation. Carboxylato-bound oxochromium(V) ion oxidizes the organic sulfides[21] to the corresponding sulfoxides but less efficiently, and the reaction is of total second-order, first-order in each reactant. On

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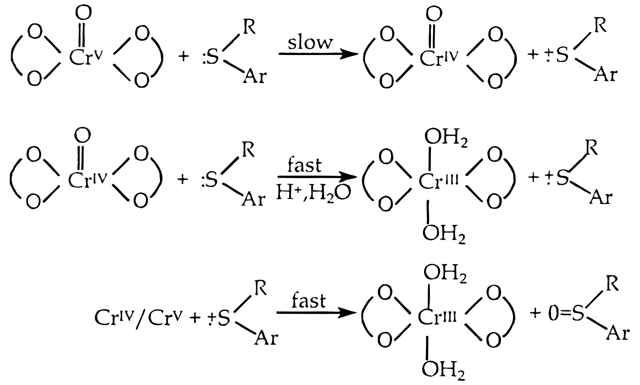
Scheme 2



the basis of the UV−vis absorption and EPR spectral studies and substituent and solvent effects, a mechanism involving an electron transfer from sulfide to Cr^V in the rate-determining step followed by fast attack of Cr^{IV}/Cr^V on the sulfide cation radical to form products has been postulated (Scheme 2).

Thus, the inference is that the nature of the ligand alters the mechanism of the reaction. It is interesting to note the difference in the reactivity of two different Cr(V) complexes toward the same substrate, organic sulfide. The carboxylato-bound complex carries a negative charge, whereas the salen complex carries a positive charge though both complexes have essentially the similar square-pyramidal configuration about the Cr^V center. Note that the relevant chromium−oxygen bond distance in both complexes is similar (1.55 Å).[42] Though we expect similar rate constants for the oxidation of same substrate with these two structurally similar oxochromium(V) complexes, substantially higher rate constant is observed with Cr^V−salen complex compared to carboxylato-bound chromium(V). To account for this large difference in reactivity different mechanisms are proposed, the electrophilic attack of oxygen at the sulfur center for the former and electron transfer from the sulfide to Cr(V) in the latter. The higher reactivity of cationic oxo(salen) Cr^V complex compared to that of anionic carboxylato bound Cr^V complex seems to support the suggested electrophilic oxygen transfer mechanism for the titled reaction. Similar behavior has been observed in the Mo^{VI} oxidation of thioethers.[43]

Experimental Section

The ligands salen, salprn, salophen, and 7,7′-Me_2salen and Cr^{III} complexes of these ligands were synthesized using established procedures.[6,8,16] The purity of ligands and Cr^{III} complexes was checked by spectral methods. Iodosylbenzene was prepared by alkaline hydrolysis of iodosobenzene diacetate according to the reported method.[44] The oxo(salen)chromium(V) complexes **1a**−**d** were obtained 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 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 oxochromium(V) salts. The aryl methyl sulfides were obtained from known synthetic methods, and dialkyl sulfides (Aldrich) were used without further purification. All other reagents were of AnalaR grade or used after purification. The kinetic study of the reaction was performed after confirming the purity of reactants and solvents used in this system.

Kinetic Measurements. A JASCO UV−vis spectrophotometer (model 7800) was employed to record the absorption spectra of Cr^{III} and $O{=}Cr^V$ complexes used in the present study and to follow the kinetics of oxygen atom transfer reactions of $O{=}Cr^V$ complexes with organic sulfides. The kinetic studies were carried out in CH_3CN under pseudo-first-order conditions with a sulfide, $O{=}Cr^V$ complex ratio of at least 10:1. The progress of the reaction was monitored by following the decay of absorbance of $O{=}Cr^V$ complex at definite time intervals at the following wavelengths ($\lambda^{ab}{}_{max}$) $[O{=}Cr^V(salen)]^+PF_6^-$, 571 nm, $[O{=}Cr^V(salen)]^+ClO_4^-$, 560 nm, $[O{=}Cr^V\text{-}(salprn)]^+ClO_4^-$, 570 nm, $[O{=}Cr^V(salophen)]^+ClO_4^-$, 600 nm, $[O{=}Cr^V(7,7\text{-}Me_2\text{-}salen)]^+ClO_4^-$, 610 nm. The reaction was followed up to 4 half-life periods.

The pseudo-first-order rate constant (k_1) for each kinetic run was evaluated from the slope of linear plot of log o.d. vs time by the method of least squares. The linearity of each fit is confirmed in terms of the values of correlation coefficient (r) and standard deviation(s). The second-order rate constant (k_2) is evaluated from the relation $k_2 = k_1$/[sulfide]. The precision of k values in all the kinetic runs is given in terms of 95% confidence limit (CL) of the student's t test. The thermodynamic parameters, the enthalpy($\Delta H^\ddagger$) and entropy ($\Delta S^\ddagger$) of activation, were evaluated by the least-squares method from the linear plot of log k_2/T vs $1/T$. The precision of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values was calculated using the method of Petersen et al.[45]

Stoichiometry and Product Analysis. The stoichiometry of the reaction between $O{=}Cr^V$(salen) complex and sulfides was studied by taking different ratios of concentration of oxidant and substrate and was found to be 1:1 and represented by eq 8

$$O{=}Cr^V(salen) + RSR' \rightarrow Cr^{III}(salen) + RSOR' \qquad (8)$$

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 1−3 h depending upon the nature of sulfide and complex (vide infra). After the removal of the solvent under reduced pressure, the organic product was extracted with ether and dried and the solvent 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 (ArSOMe) having S=O stretching frequency in the characteristic region 1070−1030 cm^{-1}. The GC analysis of the product also indicated 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 complex as the products.

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