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Oxygenation Reaction of Organic Sulfides with Oxochromium(V) Ion

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The selective oxidation of 19 alkyl aryl sulfides to sulfoxides with three oxochromium(V) complexes in an acetonitrile−water mixture is overall second order, first order in the oxidant and in the substrate. Sulfides containing electron-attracting substitutents retard the rate while those containing electron-releasing substitutents accelerate the rate of oxidation. The rate constant for the oxygenation reaction, k_2, is better correlated with σ^+/σ^- than Hammett σ constants. The reactivity of different alkyl phenyl sulfides C_6H_5SR (R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, and *t*-Bu) is accounted for in terms of Taft's polar, σ^*, and steric, E_s, substitutent constants. These kinetic results are interpreted in terms of a mechanism involving outer sphere electron transfer from sulfide to Cr(V) as the rate-determining step. The results of Cr(V) oxidation are compared with those of Cr(VI) oxidation.

Introduction

The chemistry of chromium is characterized by the large number of available oxidation states and the formation of oxo complexes.[1] Chromium(V) has been reported as the intermediate oxidation state in the reaction of chromium(VI) with organic compounds and cellular systems.[2−4] Further, Cr(V) has recently been shown to react rapidly with DNA, and therefore, it may be the active species responsible for chromium(VI)-induced carcinogenic effects.[5−10] The Cr(V) complexes have also been used as efficient oxidants for inorganic and organic substrates.[11−15] The isolation of relatively stable Cr(V) complexes has led to a number of detailed studies into the structure and redox chemistry of Cr(V).[15−25] These stable water-soluble chromium(V) complexes require chelation of hydroxy acids, Schiff bases, or sugars. One of the stable classes of chromium(V) complexes is that obtained in the reaction of tertiary α-hydroxyalkanoic acids with chromium trioxide.[13] For the present study, we have used three carboxylato-bound chromium(V) complexes, I−III (Figure 1), for the oxidation of organic sulfides. In complexes I−III, chromium(V) oxidation state is stable enough to permit spectroscopic and crystallographic studies.[21−26]

Though a large variety of reagents have been utilized for the oxidation of alkyl aryl sulfides, the recent interest is on the use of transition-metal-based oxidants.[27−39] Further, though chromium−sulfur interaction is of bio-

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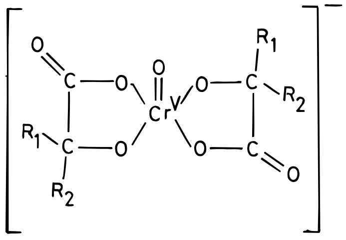

Complex I : $R_1 = R_2 = CH_3$
II : $R_1 = CH_3$
$R_2 = C_2H_5$
III : $R_1 = R_2 = C_2H_5$

Figure 1. Chromium(V) complexes I−III.

logical importance, little effort has been made to understand the mechanism of such reactions.[2,9,30,31,40]

Herein, we report our results of detailed kinetic study on the redox reactions of three chromium(V) complexes with 19 alkyl aryl sulfides. The three oxochromium(V) complexes used are sodium bis(2-hydroxy-2-methylpropionato)oxochromium(V) (complex I), sodium bis(2-hydroxy-2-methylbutyrato)oxochromium(V) (complex II), and sodium bis(2-ethyl-2-hydroxybutyrato)oxochromium(V) (complex III).

Results and Discussion

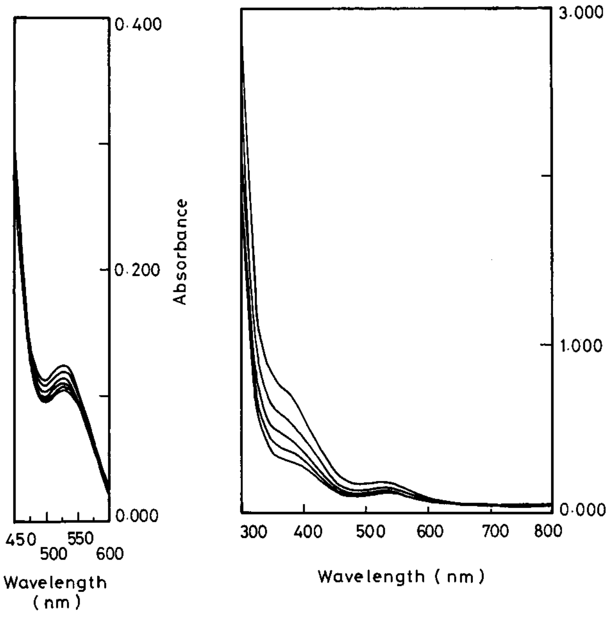

Figure 2. Decay of oxochromium(V) complex(III) (0.001 M) in the presence of methyl phenyl sulfide (0.01 M), taken at an interval of 5 min.

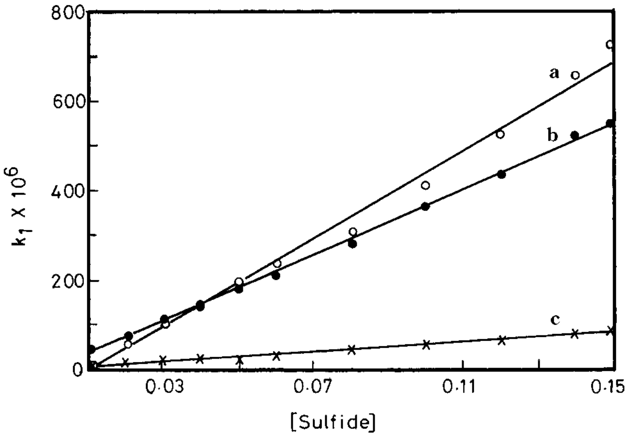

Figure 3. Plots of pseudo-first-order rate constant, k_1, versus [MPS] for the oxidation with oxochromium(V): (a) complex I, (b) complex II, and (c) complex III in 80% CH_3CN:20% H_2O (v/v) at 303 K.

The kinetic study was carried out spectrophotometrically under pseudo-first-order conditions in the presence of excess of sulfide over Cr(V) in an 80:20 (v/v) acetonitrile−water mixture by measuring the decrease in absorbance at 540 nm. The Cr(V) complexes have an absorption maximum at 510 nm in aqueous medium, which is shifted to 540 nm in the presence of acetonitrile. A similar shift in λ_{max} has also been noted by Rajavelu and Srinivasan.[40] A sample run for the reaction of methyl phenyl sulfide (MPS) with complex III is shown in Figure 2. The oxidation of MPS at 30 °C is first order in oxidant, as evidenced from the linearity of $\log(A_\infty - A_t)$ versus time plots, as well as from the constancy of first-order rate constants, k_1, obtained at different [Cr(V)]. The k_1 value is sensitive to the change of [MPS] and varies linearly with [MPS] (Figure 3). The second-order rate constant, $k_2 = k_1$/[MPS], remains almost constant, indicating that the reaction is also first order with respect to sulfide. Similar results are observed for the oxidation of sulfides with all three oxochromium(V) complexes (Figure 3).

The stability of oxochromium(V) complexes depends on the pH of the solution, and the maximum stability is in the pH range 3−4. In alkaline medium, these chromium(V) complexes undergo instant disproportionation and at pH < 3, the percentage of available Cr(V) is low. All the data reported in the present study have been measured at pH 3, unless otherwise stated, by adding the appropriate amount of perchloric acid. These complexes are highly stable in aprotic solvents.[22,24] Stock solutions of Cr(V) complexes are generally prepared in acetonitrile and are used on the same day of preparation. Even in

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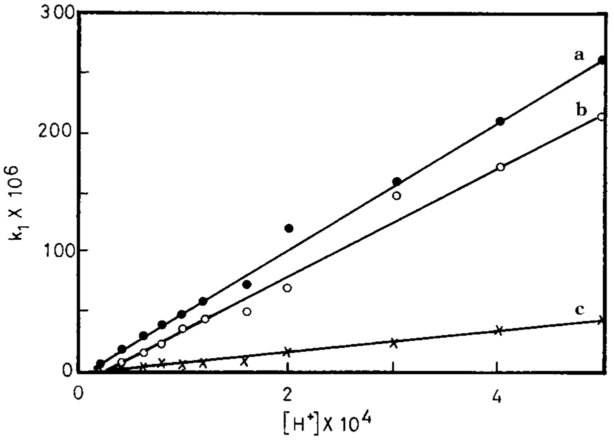
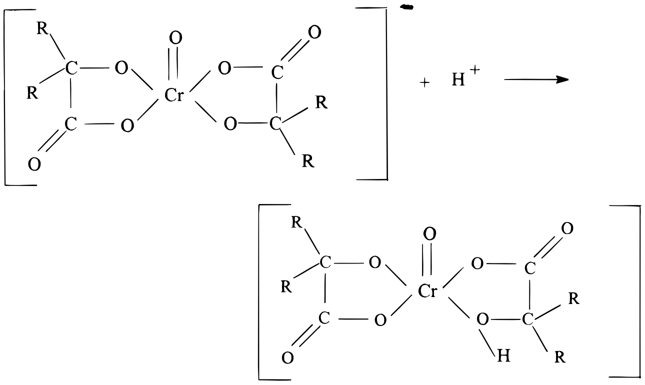


Figure 4. Plots of pseudo-first-order rate constants, k_1, versus $[H^+]$ for the oxidation of MPS with oxochromium(V): (a) complex I, (b) complex II, and (c) complex III in 80% CH_3CN: 20% H_2O (v/v) at 303 K.

the present experimental conditions, the complexes undergo slow self-decomposition. The self-decomposition of complexes I–III under the present experimental conditions has the rate constants (1.30, 0.988, and 0.121) × 10^{-6} s^{-1}, respectively. These values are very small compared to the values observed in the presence of sulfide, and the k_1 values listed in all tables are the rate constants for the oxidation of sulfides only, i.e., the self-decomposition rate constant has been subtracted from the observed rate constant for the Cr(V) oxidation of sulfides. To understand the effect of acid on the reactivity of these reactions, $[H^+]$ was varied in the range (0.2–40.0) × 10^{-4} M, and the rate constants at different $[H^+]$ are shown in Figure 4. The reaction is catalyzed by acid, and it is first order in H^+, estimated from the plot of log k_1 versus log$[H^+]$. The acid catalysis of the redox reaction can be explained with the knowledge that protonation of Cr(V) complex, as shown below,



makes the oxidant more electrophilic, thereby facilitating electron acceptance from sulfides at high $[H^+]$. The resulting protonated complex would presumably be a stronger oxidant and more reactive than its deprotonated counterpart. A similar explanation has been offered for the acid catalysis in the Cr(VI) oxidation of organic sulfides.[2,35]

The increase in acetonitrile content of the medium decreases the rate constant, k_1 (Table 1). A plot of log k_1 versus $1/D$ is fairly linear with a negative slope, indicating the involvement of a negative ion as one of the reactants in the rate-determining step.[41] Though the reaction is sensitive to the change of solvent composition, the change in the k_2 values with the change in the percentage of acetonitrile from 30 to 100 is comparatively small and is in the range of 3–5 times. This small solvent effect can be taken in favor of electron transfer in the rate-determining step. The solvent effect is substantial in the oxidation of aryl methyl sulfides by (diacetoxyiodo)benzene,[42] peroxodisulfate ion,[43] periodate ion,[44] and peroxomonosulfate ion,[45] and the solvent effect has been taken as evidence for the nucleophilic substitution in the rate-determining step of these reactions.

Table 1. Effect of Varying Solvent Composition on Cr(V) Oxidation of MPS at 303 K

$[Cr(V)] = 0.001$ M $[MPS] = 0.01$ M $[H^+] = 0.001$ M

	$k_2 \times 10^3$ M^{-1} s^{-1}		
CH_3CN–H_2O	complex I	complex II	complex III
30–70	11.5 ±0.17	10.1 ± 0.09	1.33 ± 0.06
40–60	9.32 ± 0.15	9.16 ± 0.08	1.00 ± 0.07
50–50	7.48 ± 0.10	7.22 ± 0.03	0.858 ± 0.10
60–40	6.44 ± 0.04	5.59 ± 0.11	0.764 ± 0.03
70–30	5.46 ± 0.19	4.39 ± 0.05	0.676 ± 0.09
80–20	4.80 ± 0.07	3.58 ± 0.06	0.601 ± 0.05
90–10	4.47 ± 0.05	2.44 ± 0.07	0.519 ± 0.11
100–0	3.29 ± 0.07	1.81 ± 0.03	0.373 ± 0.01

A: Substituent Effects. To gain insight into the mechanism of the reaction, the influence of introducing the electron-releasing and electron-withdrawing substituents in the *meta-* and *para-*positions of the phenyl ring of PhSMe on the rate of oxidation has been investigated. Though the k_2 value varies with the nature of the substituent in the phenyl ring of ArSMe, in all cases the order with respect to sulfide is found to be one. The oxidation reaction has been followed at three different temperatures, and the values of the rate constants at 20, 30, and 40 °C but at constant $[H^+]$ and ionic strength for the Cr(V) (complex III) oxidation of MPS and several *meta-* and *para-*substituted phenyl methyl sulfides are given in Table 2.

The electron-releasing substituents in the benzene ring accelerate the rate while electron-attracting substituents produce the opposite effect. The thermodynamic parameters, the enthalpy ($\Delta H^{\ddagger}$), and the entropy ($\Delta S^{\ddagger}$) of activation are listed in Table 2 along with the k_2 values. A similar substituent and temperature dependence study was performed for oxochromium(V) complexes I and II also. In these cases also the electron-releasing and the electron-attracting substituents produce the similar substituent effect.

As this redox reaction is of total second order, first order each in the oxidant and the substrate, k_2 values can be used as such to evaluate the reaction constant, ρ, from the Hammett equation. Though the correlation of log k_2 with Hammett's substituent constants (σ) is only fair ($\rho = -1.89$, $r = 0.954$, $n = 14$ at 303 K), a substantial improvement in the correlation is realized if σ^+/σ^- values are used ($\rho^+ = -1.19$, $r = 0.972$, $n = 14$ at 303 K, Figure 5). A plot of log k_2 with oxidation potentials of aryl methyl sulfides is linear with a good correlation coef-

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Table 2. Second Order Rate Constant, k_2, Values at Three Different Temperatures and Enthalpy, Entropy, and Free Energy of Activation for the Cr(V) (Complex III) Oxidation of Aryl Methyl (X = C_6H_4SMe) and Alkyl Phenyl (C_6H_5SR) Sulfides in 80:20 Acetonitrile:Water (v/v)

$[Cr(V)] = 0.001$ M $[\text{sulfide}] = 0.01$ M $[H^+] = 0.001$ M

	$k_2 \times 10^4$ M^{-1} s^{-1}					
X	293 K	303 K	313 K	$\Delta H^‡$ (kJ mol^{-1})	$-\Delta S^‡$ (J K^{-1} mol^{-1})	$\Delta G^{‡\,a}$ (kJ mol^{-1})
H	3.89	6.01	8.96	29.0	249	105
p-OMe	78.5	116	186	30.1	221	97.1
p-Me	24.0	31.5	51.0	25.9	245	100
p-Et	18.6	26.0	41.0	27.4	242	101
p-iPr	21.1	28.5	45.5	26.5	244	101
m-Me	9.85	14.1	25.1	32.8	229	102
p-F	6.45	9.05	14.5	28.1	249	103
m-OMe	4.00	5.75	8.50	26.0	260	105
p-Cl	3.55	4.90	7.95	27.9	254	105
p-Br	3.60	5.55	8.45	29.7	248	105
m-Cl	2.95	4.15	6.60	27.9	256	106
p-COOH	1.15	1.61	2.62	28.6	261	107
p-COMe	1.06	1.54	2.56	30.8	254	108
p-NO_2	0.455	0.655	1.05	29.1	267	110
R						
Et	3.50	5.46	8.83	32.7	238	105
Pr	3.42	5.18	8.35	31.5	242	105
n-Bu	3.06	4.51	7.43	31.2	244	105
i-Pr	3.04	4.28	6.93	28.8	252	105
t-Bu	0.466	0.667	1.23	34.4	249	110

[a] At 303 K.

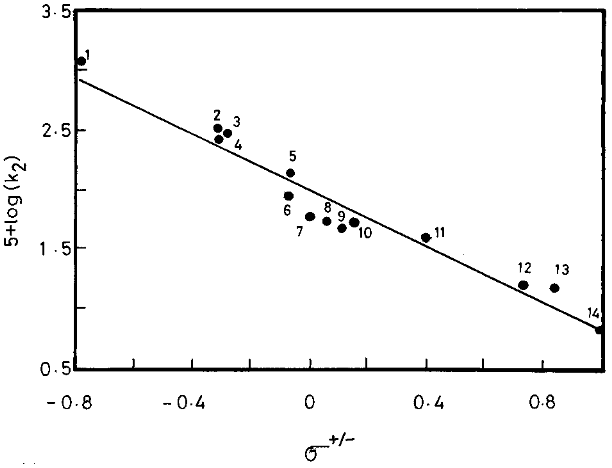

Figure 5. Hammett plot (log *k* versus σ^+) for the oxidation of substituted phenyl methyl sulfides by oxochromium(V) complex III. The points are as follows: (1) *p*-OMe, (2) *p*-Me, (3) *p*-Et, (4) *p*-*i*-Pr, (5) *m*-Me, (6) *p*-F, (7) *m*-OMe, (8) H, (9) *p*-Cl, (10) *p*-Br, (11) *m*-Cl, (12) *p*-COOH, (13) *p*-COMe, (14) *p*-NO_2.

ficient ($r = 0.985$, $n = 9$, Figure 6). A fair correlation was also obtained for a plot of log k_2 with the first ionization energy of sulfides ($r = 0.966$, $n = 6$). (As the oxidation potentials and ionization energies of all sulfides used in the present study are not available in the literature, only the available values have been used in the correlation.) These results point out the development of partial positive charge on sulfur of ArSR in the transition state and the importance of resonance between the substitutent and the reaction center. The better correlation of log k_2 with σ^+ rather than σ and the low magnitude of the ρ^+ value have been taken as kinetic evidence for the electron-transfer mechanism in the oxidation of organic sulfides.[46] Further, the plots of log k_2 versus oxidation potential/ionization energy of sulfides are linear (Figure 6), which provides additional support for the electron-transfer mechanism in the oxidation of organic sulfides by oxochromium(V).

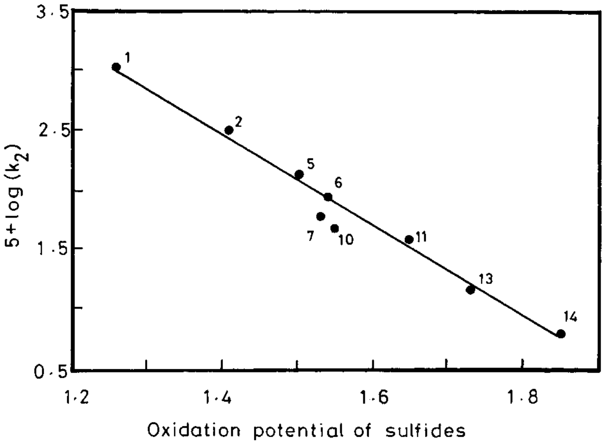

Figure 6. Plots of log k_2 versus oxidation potential of sulfides for the oxidation of substituted phenyl methyl sulfides by oxochromium(V) complex III. The points are referred to by the same numbers as in Figure 5.

(B) Steric Effects in the Oxidation of Alkyl Phenyl Sulfides. Studies with different alkyl phenyl sulfides show that the rate decreases in the order PhSMe > PhSEt > PhS-*n*-Pr > PhS-*n*-Bu > PhS-*i*-Pr > PhS-*t*-Bu (Table 2). In all these cases, the overall order of the reaction was found to be second order, first order both in the oxidant and substrate. If the inductive effect of the alkyl group predominates, then the reverse order of reactivity should have been observed. To understand the role of steric effects, the kinetic data are analyzed with multiparametric Taft's equation,[47] and the results are shown in eqs 1−3.

$$\log k_2 = 1.69 - 1.20\sigma^* + 0.816E_s \quad (r = 0.977, \text{ at } 293\text{ K}) \quad (1)$$

$$\log k_2 = 1.79 - 1.02\sigma^* + 0.807E_s \quad (r = 0.983, \text{ at } 303\text{ K}) \quad (2)$$

$$\log k_2 = 1.96 - 1.27\sigma^* + 0.786\,E_s \quad (r = 0.979, \text{ at } 313\text{ K}) \quad (3)$$

The negative value of ρ^* is similar to the ρ^+ value observed for the oxidation of the substituted phenyl methyl sulfides. These results indicate the importance of both polar and steric effects in the Cr(V) oxidation of organic sulfides.

(C) Mechanism of Oxidation. The overall second-order nature of reaction leads to the formulation of rate law (eq 4).

$$-\frac{d[Cr(V)]}{dt} = k_2[Cr(V)][MPS] \quad (4)$$

Direct spectroscopic evidence for the formation of chromium(IV) intermediate was not obtained. The EPR spectral study of the reaction at room temperature did not give evidence for organic radical formation. But the

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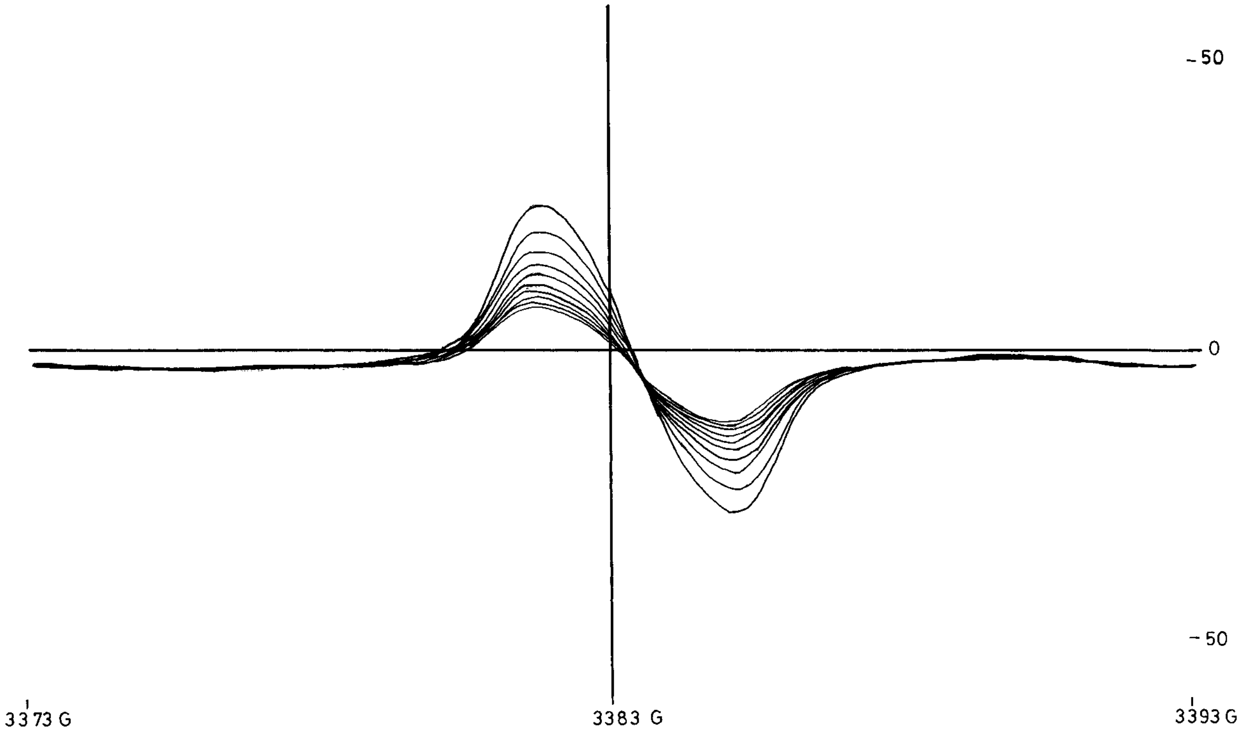


Figure 7. Decay of EPR signal intensity of oxochromium(V) complex (III) (0.001 M) in the presence of methy phenyl sulfide (0.01 M), taken at an interval of 5 min.

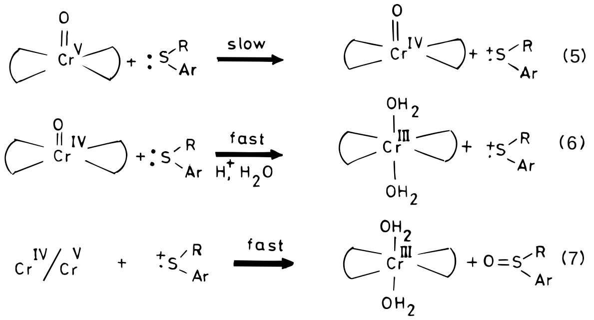
signal due to Cr(III) appeared not immediately but after a time gap with respect to Cr(V) signal. Therefore, we presume that the Cr(IV) intermediate might have formed, as it is EPR silent, and the organic radical might have reacted with rates faster than the EPR time scale. Wetterhahn has recently proven that these Cr(V) complexes do not show formation of carbon-based or oxygen radicals in the pH range of 3−4.[9] Wetterhahn has also pointed out that in the reaction between Cr(V) (complex III) and thymidine nucleotides the Cr(IV) is the active species rather than Cr(V).[9]

To get a clue on the mechanism of the reaction, the kinetics of the reaction has also been followed by EPR spectroscopy. The change of intensity of EPR signal of Cr(V) with time is shown in Figure 7 and the rate constant obtained for the oxidation of MPS is 6.0×10^{-4} M^{-1} s^{-1}, which is close to the value observed by spectrophotometric technique. As the EPR spectrum of Cr(III) is very broad, we find it difficult to get a reliable rate constant for the rate of formation of Cr(III) from the EPR spectra.

The observed second-order kinetics, better correlation of log k_2 with σ^+/σ^- rather than Hammett's σ, and the formation of the EPR signal of the Cr(III) complex after a time gap led us to postulate an outer-sphere electron-transfer mechanism (Scheme 1) for the carboxylato-bound chromium(V) oxidation of organic sulfides.

The mechanism of oxidation of alkyl aryl sulfides by oxochromium(V) complexes I−III (Scheme 1) can be summarized as follows. The first step involves an electron transfer from the organic sulfide to oxochromium(V) ion to form sulfide cation radical and Cr(IV). As Cr(IV) is more reactive than the Cr(V) complex,[25,26,48] the intermediate Cr(IV) may react with another molecule of sulfide to form Cr(III) and sulfide cation radical. The formation of sulfoxide may be due to the reaction between the sulfide cation radical with Cr(V) or Cr(IV) complex. A similar product formation step has been proposed in the Cr(VI) oxidation of organic sulfides and sulfoxides.[2,49] The linear relationship between log k_2 of various substituted thioanisoles and oxidation potential/first ionization energy may be taken as kinetic evidence for electron transfer in the rate-controlling step. The rate constant for this electron-transfer reaction was also calculated by applying the Marcus theory of electron transfer.[50] There is fairly good agreement between the calculated and the experimental values (the calculated and experimentally observed k_2 values for the oxidation of $C_6H_5SCH_3$ are 2.10×10^{-4} and 6.01×10^{-4} M^{-1} s^{-1}, respectively). This successful application of Marcus theory to the present redox system also supports an electron-transfer mechanism for the Cr(V) oxidation of organic sulfides.

Scheme 1



(D) Comparison with Cr(VI) Oxidation of Alkyl Aryl Sulfides. The oxidation of MPS and substituted

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phenyl methyl sulfides by Cr(VI) in aqueous acetic acid and in aqueous acetonitrile has been reported from this laboratory, and the results in both media are similar.[2,34,35] Both the Cr(VI) and Cr(V) oxidation of sulfides follow total second-order kinetics, first order with respect to the sulfide as well as with the oxidant. In both Cr(V) and Cr(VI) oxidation, electron-releasing groups in the benzene ring accelerate the rate while the electron-attracting groups retard the rate. The rate of the reaction is highly dependent on the pH of the medium, and the increase in [H^+] increases the rate in both Cr(V) and Cr(VI) oxidation of organic sulfides. There is a good correlation between log k_2 with oxidation potential/ionization energy in both oxidations. Further, the plots of log k_2 with σ as well as with σ^+/σ^- are of comparable success with Cr(VI) oxidation. On the other hand, substantial improvement in the correlation is observed if σ^+/σ^- values are used rather than Hammett's σ constants in Cr(V) oxidations. An initial increase in the water content of the medium decreases the rate in the Cr(VI) oxidation,[2,35] whereas an increase in water content of the medium increased the rate of oxidation in the Cr(V) oxidation of sulfides. A plot of log $k_{(\mathrm{Cr(VI)})}$ versus log $k_{(\mathrm{Cr(V)})}$ is attempted, and the plots are found to be linear with the slope equals to unity. These comparable results speculate the operation of similar mechanism for both Cr(V) and Cr(VI) oxidation of sulfides.

Experimental Section

Sodium bis(2-hydroxy-2-methylpropionato)oxochromium(V) (complex I), sodium bis(2-hydroxy-2-methylbutyrato)oxochromium(V) (complex II), and sodium bis(2-ethyl-2-hydroxybutyrato)oxochromium(V) (complex III) were synthesized from their corresponding ligand acids and sodium dichromate (Merck, AR grade) in acetone and hexane (Merck, AR grade) as described elsewhere.[13,21] *Caution! Cr(VI) is a known human carcinogen, and Cr(V) complexes are mutagenic and potentially carcinogenic. Due care must be taken to avoid breathing dusts of the compounds and contact with skin.* The ligand acids 2-hydroxy-2-methylpropionic acid (HMPA) (Fluka 99%), 2-hydroxy-2-methylbutyric acid (HMBA) (Aldrich 99%), and 2-ethyl-2-hydroxybutyric acid (HEBA) (Aldrich 99%) and solvents such as acetone, *n*-hexane, and chloroform (Merck, spectroscopic grade) were used as received. Spectroscopic-grade solvent acetonitrile and doubly distilled water were used throughout the course of the present study. All the alkyl aryl sulfides have been prepared by known procedures[2,35] and purity checked by usual methods. All other reagents used were of AnalaR grade.

The kinetics of the reaction was followed by measuring the decrease in absorbance at 540 nm (ϵ_{540} values of Cr(V) complexes I–III are 161, 170, and 169 $M^{-1}\,cm^{-1}$, respectively), employing a Hitachi-200 model UV–vis spectrophotometer.[13] Though the absorption maximum for the Cr(V) complex in aqueous solution is 510 nm, in the presence of acetonitrile the $\lambda_{\max}$ is shifted to 540 nm. A similar shift in $\lambda_{\max}$ due to the change of medium from aqueous to acetonitrile was noticed by Rajavelu and Srinivasan in Cr(V) oxidation of lactic and thiolactic acids.[40] The purity of chromium(V) complexes was checked both by iodometric methods and by the method developed by Krumpolc and Rocek.[51] In all the rate studies, pseudo-first-order conditions were maintained by keeping the concentration of sulfide:oxidant in a minimum ratio of 10:1. The method of calculation of k_1, k_2, and activation parameters and their precision are described in our previous reports.[35,38]

EPR spectra was recorded on a Varian E112-ESR spectrometer operating at ~9.4 GHZ and at 20 mW microwave power. All EPR recordings were performed at room temperature (298 K), and the frequency was measured with a wavemeter indirectly calibrated via the resonance of DPPH (g = 2.0036).

Product Analysis. The reaction mixture from an actual kinetic run in the oxidation of MPS (and other sulfides) by complex III was extracted with chloroform and dried over anhydrous sodium sulfate. Chloroform was removed under reduced pressure, and the residue was analyzed by IR spectroscopy, HPLC, and TLC. In TLC analysis, the residue was eluted with 80:20 benzene–ethyl acetate (v/v) solvent mixture. The reaction mixture gave two spots of R_f values 0.34 and 0.95 corresponding to methyl phenyl sulfoxide and methyl phenyl sulfide, respectively. The R_f values for *p*-methoxyphenyl methyl sulfide and its corresponding sulfoxide are found to be 0.95 and 0.36, respectively. R_f values of 0.97 and 0.29 are obtained for *p*-chlorophenyl methyl sulfide and its sulfoxide, respectively.

The chloroform extract was also analyzed by HPLC after the solvent was evaporated. HPLC samples were eluted using 80% methanol:20% water (v/v) at a elution rate of 2 mL per minute. The retention time obtained for sulfides was almost in the range of 2.40. The retention time for methyl phenyl sulfoxide was 5.9 and for *n*-propyl phenyl sulfoxide was 10. A similar HPLC analysis was carried out for the entire set of substrates used in the present study.

The chloroform extract of the product was also analyzed using infrared spectroscopy. The stretching frequency in the region 1070–1030 cm^{-1} was obtained in all cases, indicating the formation of sulfoxide. These experimental observations point out that under the present experimental conditions sulfides are oxidized up to sulfoxide stage only.

The reaction mixture of MPS and Cr(V) complex III was buffered by a mixture of perchloric acid and sodium perchlorate. This was allowed to react for 5–6 h at room temperature and then subjected to ion-exchange chromatography. Separation was carried out with the use of BIO-Rad 50 W-X_2 sulfonate resin, H^+ form, 200–400 mesh, column length 5 cm, column capacity 2.0 mequiv. The Cr(III) products passed unchanged through anion-exchange resin but were absorbed into cation-exchange resin. A green elute passed through the column quickly. The elute was analyzed using absorption spectroscopy. The extinction coefficients (ϵ_{588} = 49 $M^{-1}\,cm^{-1}$; ϵ_{415} = 61 $M^{-1}\,cm^{-1}$) of the Cr(III) product and the ease with which it was eluted from the sulfonate cation-exchange column indicate the principal reduction product to be a unipositive bischelated complex of chromium(III). This elute constituted between 60 and 70% of Cr(V) taken. Fanchiang et al.[25] have tabulated the spectral properties of a number of known carboxylato-bound chromium(III) complexes with those of the Cr(III) products formed during the reduction of Cr(V) chelate complex III. A second band was rapidly eluted with 0.5 M $HClO_4$ and exhibited peaks at 581 nm (ϵ = 37 $M^{-1}\,cm^{-1}$) and 414 nm (ϵ = 48 $M^{-1}\,cm^{-1}$), which was identified to be $[Cr(H_2O)_6]^{3+}$. Studies with other oxochromium(V) complexes yielded similar results.

Stoichiometry. Estimation of the unreacted Cr(V) from the reaction mixture where [Cr(V)] > [sulfide] after the completion of the reaction showed that one molecule of sulfide is oxidized for each Cr(V) species reduced to Cr(III). The stoichiometry of the reaction is represented by eq 8.

$$\mathrm{Cr^{V}{=}O + PhSMe \rightarrow Cr^{III} + PhSOMe} \qquad (8)$$

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