equipped with a rubber septum and magnetic stirring bar was placed 142 mg (0.33 mmol) of diester **55**. The system (cooled to 0 °C) was charged with 7.17 mL (0.66 mmol) of 0.092 M potassium hydroxide in methanol, and the solution was stirred for 5.5 h, during which time the ice bath melted and the cooling bath was maintained at 10–20 °C. After being warmed to room temperature and stirred for a further period of 40 min, the reaction mixture was diluted with 70 mL of ether and washed with 10 mL of brine and 10 mL of water. The combined aqueous washings were extracted with 25 mL of ether, the combined organic fractions were dried over magnesium sulfate, and the solvent was removed with a rotary evaporator. The crude material (140 mg) was purified by column chromatography (6 g of silica gel) with 1:2 ether/hexanes as the eluant to obtain 92.4 mg (quantitative yield) of **5** as a white crystalline solid. This material was recrystallized from spectrophotometric grade pentane by slow evaporation at room temperature to afford small white needles: mp 64.5–65.5 °C; $[\alpha]^{25}_D$ +328° (c 0.42, CHCl$_3$); ^{1}H NMR δ 0.89 (t, 3 H, J = 7.4), 0.99 (d, 3 H, J = 7.0), 1.14 (d, 3 H, J = 7.0), 1.40–2.64 (complex, 11 H), 3.58 (t, 1 H, J = 10), 3.79 (dd, 1 H, J = 4.5, 10), 5.20 (m, 1 H), 5.58 (m, 1 H), 5.76 (dd, 1 H, J = 5.4, 9.7), 5.99 (d, 1 H, J = 9.7). Anal. Calcd for C$_{17}$H$_{26}$O$_3$: C, 73.34; H, 9.42. Found: C, 73.19; H, 9.26. The stereostructure of **5** was verified by single-crystal X-ray analysis.

(1R,2R,8R,8aS)-1-(Hydroxymethyl)-2-methyl-8-[(S)-(2-methylbutyryl)oxy]-1,2,6,7,8,8a-hexahydronaphthalene (50). This compound was prepared from diester **56** by the procedure described for the preparation of alcohol **5**. After purification by column chromatography, the compound was obtained as white crystals: mp 78–82 °C, $[\alpha]^{25}_D$ –342 °C (c 0.54, CHCl$_3$); ^{1}H NMR δ 0.90 (t, 3 H, J = 7.4), 0.98 (d, 3 H, J = 7), 1.14 (d, 3 H, J = 7)8 1.14 (d, 3 H, J = 7), 1.26 (br s, 1 H), 1.45 (m, 1 H), 1.67 (m, 2 H), 1.95–2.63 (complex, 7 H), 3.58 (dd, 1 H, J = 10), 3.77 (dd, 1 H, J = 4.4, 10), 5.21 (br s, 1 H), 5.58 (m, 1 H), 5.76 (dd, 1 H, J = 5.9, 9.7), 5.99 (d, 1 H, J = 9.7). Anal. Calcd for C$_{17}$H$_{26}$O$_3$: C, 73.34; H, 9.42. Found: C, 73.55; H, 9.44.

Supplementary Material Available: Experimental details containing positional thermal parameters of non-hydrogen atoms, bond lengths, bond angles, and torsion angles for compound **5** (10 pages). Ordering information is given on any current masthead page.

Mechanism of the Oxidation of Alkyl Aryl and Diphenyl Sulfides by Chromium(VI)

Chockalingam Srinivasan,* Arunachalam Chellamani, and Seenivasan Rajagopal

School of Chemistry, Madurai Kamaraj University, Madurai-625 021, India

The mechanism of Cr(VI) oxidation of organic sulfur compounds has been investigated by studying the rates of oxidation of 17 alkyl aryl sulfides and 6 diphenyl sulfides respectively in 50% (v/v) aqueous acetic acid and 75:25 acetic acid–water (v/v) mixtures. The oxidation follows second-order kinetics at constant [H$^+$] and ionic strength. Those sulfides containing electron-releasing groups in the benzene ring accelerate the rate while those with electron-attracting groups retard the rate. A good correlation is found to exist between log k_2 and Hammett σ constants for both aryl methyl and diphenyl sulfides. The excellent correlations obtained between log k values and oxidation potentials/ionization energies and the absence of any retardation on the rate of oxidation in the presence of Mn(II) suggest that the mechanism presumably involves a one-electron-transfer process. That the oxidation is susceptible to steric congestion at the reaction center, sulfur, has been revealed by the excellent correlation between the logarithm of rate coefficients of alkyl phenyl sulfides, C$_6$H$_5$SR (R = Me, Et, n-Pr, i-Pr, and t-Bu) and Taft's steric substituent constant, E_s.

Although chromium(VI) is widely used as an oxidant in the preparation of sulfoxides[1] from the corresponding sulfides, the formulation of a detailed mechanism for this reaction is impeded by the lack of kinetic data. In spite of the extensive studies on the mechanism of the oxidation of sulfides to sulfoxides by several oxidants like peroxydisulfate ion,[2] peroxydiphosphate ion,[3] bromine,[4] hydrogen peroxide,[5] peroxybenzoic acid,[6] (diacetoxyiodo)benzene,[7]

chloramine-T,[8] bromamine-T,[8] and chlorine,[9] kinetics of oxidation by metal ion oxidants has received little attention. However, the oxidation of alkyl phenyl sulfides by Mn^{3+} has been proposed to proceed by a one-electron-transfer mechanism[10] as the rate of oxidation increases with a decrease in the values of half-wave (oxidation) potential and ionization energy.

(1) Knoll, R. *J. Prakt. Chem.* **1926,** *113,* 40. Edwards, D.; Stenlake, J. B. *J. Chem. Soc.* **1954,** 3272.

(2) (a) Arumugam, N.; Srinivasan, C.; Kuthalingam, P. *Indian J. Chem.* **1978,** *16A,* 478. (b) Kuthalingam, P. Ph.D. Thesis, Madurai Kamaraj University, Madurai, 1980. (c) Sundararajan, G. M. Phil. Thesis, Madurai Kamaraj University, 1981. (d) Srinivasan, C.; Kuthalingam, P.; Arumugam, N. *Can. J. Chem.* **1978,** *56,* 3043. (e) Srinivasan, C.; Kuthalingam, P.; Arumugam, N. *Int. J. Chem. Kinet.* **1982,** *14,* 1139.

(3) Srinivasan, C.; Kuthalingam, P.; Arumugam, N. *J. Chem. Soc., Perkin Trans. 2* **1980,** 170.

(4) Miotti, U.; Modena, G.; Sedea, L. *J. Chem. Soc. B* **1970,** 802.

(5) Modena, G.; Maioli, L. *Gazz. Chim. Ital.* **1957,** *87,* 1306.

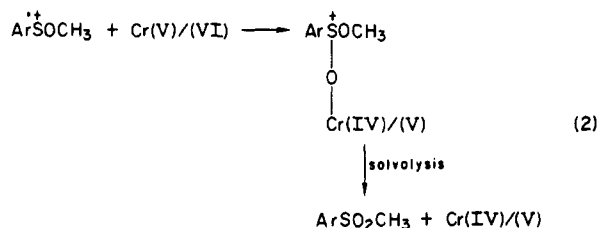(6) Colonna, F. P.; Danieli, R.; Distefano, G.; Ricci, A. *J. Chem. Soc., Perkin Trans. 2* **1976,** 306.

(7) Srinivasan, C.; Chellamani, A.; Kuthalingam, P. *J. Org. Chem.* **1982,** *47,* 428.

(8) Ruff, F.; Kucsman, A. *J. Chem. Soc., Perkin Trans. 2* **1975,** 509. **1982,** 1075.

(9) Humffray, A. A.; Imberger, H. E. *J. Chem. Soc., Perkin Trans. 2* **1981,** 382.

(10) Gilmore, J. R.; Mellor, J. M. *Tetrahedron Lett.* **1971,** 3977. Dewar, P. S.; Ernstbrunner, E.; Gilmore, J. R.; Godfrey, M.; Mellor, J. M. *Tetrahedron* **1974,** *30,* 2455.

The general conclusions[11] emerged from consideration of the reduction of Cr(VI) (HCrO₄⁻) by one-equivalent reducing agents in acidic aqueous solution is that the reduction proceeds by a sequence of one-electron steps, i.e., the first step in the reduction is from Cr(VI) → Cr(V), then Cr(V) → Cr(IV), and finally Cr(IV) → Cr(III). The comprehensive mechanistic studies based on the linear free energy relationship have suggested that in several cases one-electron-transfer process is characterized by low ρ values (−0.5 to −1.5).[12,13] The low ρ value (−0.8) observed in the Cr(VI) oxidation of aryl methyl sulfoxides to sulfones has been taken by Baliah and Satyanarayana[14] as evidence for the one-electron-transfer mechanism. The envisaged mechanism involves a cation radical intermediate which may attack the oxygen atom of Cr(VI) or Cr(V) and yield the sulfone on solvolysis. The low ρ⁺ value

$$ArSOCH_3 + Cr(VI) \longrightarrow Ar\overset{\cdot+}{S}OCH_3 + Cr(V) \qquad (1)$$

$$Ar\overset{\cdot+}{S}OCH_3 + Cr(V)/(VI) \longrightarrow \underset{\substack{| \\ O \\ | \\ Cr(IV)/(V)}}{Ar\overset{+}{S}OCH_3} \qquad (2)$$

$$\downarrow solvolysis$$

$$ArSO_2CH_3 + Cr(IV)/(V)$$

(−0.48) observed for the oxidation of diaryl sulfoxides by Cr(VI) has led us[15] to propose a mechanism analogous to the one proposed for aryl methyl sulfoxides. In the Cr(VI) oxidative cleavage of 2-aryl-1-phenylethanols[16] a ρ value of −1.06 has been considered as an indication of one-electron-transfer process. We report here details of the studies of (a) the kinetics of Cr(VI) oxidation of alkyl aryl sulfides and (b) the substituent effect in the Cr(VI) oxidation of aryl methyl and diphenyl sulfides. For this purpose we employed 25 aryl methyl, alkyl phenyl, and diphenyl sulfides. On the basis of the kinetic results, we propose a suitable mechanism for the oxidation.

Results and Discussion

Oxidation of Alkyl Aryl Sulfides. The kinetic studies were carried out under pseudo-first-order conditions in the presence of excess sulfide in 50:50 acetic acid–water (v/v) mixture. A detailed investigation with methyl phenyl sulfide (MPS) revealed that the rate of disappearance of Cr(VI) at constant [H⁺] follows second-order kinetics, eq 3, and has been confirmed by the following facts. The

$$\frac{-d[Cr(VI)]}{dt} = k_2[MPS][Cr(VI)] \qquad (3)$$

logarithm of pseudo-first-order rate constants showed a linear dependence on the log [MPS] with a slope of 1.03 ± 0.07 (r = 0.999, s = 0.01), showing that the order with MPS is unity. That the reaction is first order with respect to Cr(VI) has been confirmed by the linearity of the plot of log (a − x) vs. time and also by the constant values of pseudo-first-order rate constants at different initial con-

(11) Edwards, J. O. "Progress in Inorganic Chemistry"; Interscience: New York, 1972; Vol. 17, p 115.

(12) Bartlett, P. D.; Ruchardt, C. *J. Am. Chem. Soc.* **1960**, *82*, 1756. Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1963**, *41*, 1744.

(13) Russel, G. A.; Williamson, R. C., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 2357. Huang, R. L.; Lee, K. H. *J. Chem. Soc. C* **1966**, 935.

(14) Baliah, V.; Satyanarayana, P. V. V. *Indian J. Chem.* **1978**, *16A*, 966.

(15) Srinivasan, C.; Venkatasamy, R.; Rajagopal, S. *Indian J. Chem.* **1981**, *20A*, 505.

(16) (a) Nave, P. M.; Trahanovsky, W. S. *J. Am. Chem. Soc.* **1968**, *90*, 4755; **1970**, *92*, 1120. (b) Cohen, M.; Westheimer, F. H. *J. Am. Chem. Soc.* **1952**, *74*, 4387. Symons, M. C. R. *J. Chem. Soc.* **1963**, 4331.

Table I. Pseudo-First-Order and Second-Order Rate Constants for the Oxidation of MPS with Cr(VI) in 50% (v/v) Aqueous Acetic Acid at 35 °C[a]

10²[MPS], M	10³[Cr(VI)], M	10⁴k₁, s⁻¹	10²k₂, M⁻¹ s⁻¹
0.500	0.500	1.25 ± 0.08	2.51 ± 0.15
0.750	0.500	1.94 ± 0.12	2.58 ± 0.17
1.00	0.500	2.70 ± 0.16	2.70 ± 0.16
1.50	0.500	3.90 ± 0.10	2.60 ± 0.07
2.00	0.500	5.26 ± 0.09	2.63 ± 0.04
4.00	0.500	11.0 ± 0.50	2.75 ± 0.12
6.00	0.500	15.6 ± 1.4	2.60 ± 0.24
8.00	0.500	21.5 ± 1.6	2.69 ± 0.20
1.50	0.750	3.68 ± 0.19	2.45 ± 0.13
1.50	1.00	3.74 ± 0.11	2.49 ± 0.07
1.50	1.25	3.70 ± 0.10	2.47 ± 0.07
1.50	1.50	3.49 ± 0.06	2.32 ± 0.04
6.00	1.50	14.5 ± 1.0	2.42 ± 0.17
6.00	3.00	13.0 ± 0.90	2.17 ± 0.15
6.00	6.00	11.5 ± 0.80	1.92 ± 0.13

[a] [HClO₄] = 1.0 × 10⁻³ M; I = 5.88 × 10⁻² M. The error quoted in k is the 95% confidence limit of Student's t test.[3]

centrations of Cr(VI) (Table I).

Kinetic data for the oxidation of MPS at different ionic strengths, [HClO₄], and percentage of acetic acid are presented in Table II. The rate of oxidation is unaffected by change in ionic strength and this may presumably be due to the attack of an ion on a neutral molecule in the rate-determining step. The reaction rate increases with an increase in the concentration of HClO₄ and the order on [H⁺] is around one ([H⁺] range = 0.0398–0.3090 M, in evaluating [H⁺] the dissociation of acetic acid is also taken into account). The data in Table II show that the rate of the reaction increases with an increase in the acetic acid content in the solvent mixture and there is first-order dependence on [H⁺]. Alternatively the enhanced rate of oxidation in solutions containing a higher percentage of acetic acid may be due to the formation of the acetyl chromate ion.[16b] The acetyl group present in this ion would increase the electron-accepting power of chromium(VI). Similar observations have been reported by Wiberg[17] in the Cr(VI) oxidation of benzaldehyde and by Baliah and Satyanarayana[14] in the oxidation of methyl phenyl sulfoxide. This behavior is in striking contrast to that observed in the oxidation of alkyl aryl sulfides by the peroxydisulfate ion.[2b,c] In the latter, the rate of oxidation is accelerated by an increase in water content of the medium and this has been accounted for by the formulation of a charge-separated complex in the rate-determining step. Similar acceleration of rate with an increase in the water content of the medium has been observed in the oxidation of aryl methyl sulfides by (diacetoxyiodo)benzene[7] and in (phenylthio)acetic acids by peroxydisulfate ion,[18] and the solvent effect has been taken as evidence for the formation of a charge-separated complex in the rate-determining step in these reactions. Consequently a charge-separated complex in the rate-limiting step in the Cr(VI) oxidation of sulfides may be excluded.

(A) Substitutuent Effects. The second-order coefficients at 30, 40, and 50 °C at constant [H⁺] and ionic strength for the Cr(VI) oxidation of MPS and several meta- and para-substituted phenyl methyl sulfides are given in Table III.

Electron-releasing substituents in the benzene ring accelerate the rate while electron-attracting substituents produce the opposite effect. The activation parameters are also included in Table III. Though the relation be-

(17) Wiberg, K. B.; Mill, T. *J. Am. Chem. Soc.* **1958**, *80*, 3022.

(18) Srinivasan, C.; Pitchumani, K. *Indian J. Chem.* **1979**, *17A*, 162.

Table II. Effect of Varying [H⁺], I, and Percentage of Solvent Composition on the Rate of Oxidation[a]

$10^2[H^+]$, M	10^4k_1,[b] s⁻¹	10^2I, M	10^4k_1,[c] s⁻¹	AcOH-H₂O[d] (v/v)	$10^2[H^+]$, M	10^4k_1 s⁻¹	$10^3k(= k_1/[H^+])$
3.98	1.25 ± 0.08	4.38	1.28 ± 0.05	50–50	3.98	1.25 ± 0.0.08	3.14
4.68	1.62 ± 0.04	4.88	1.26 ± 0.05	60–40	7.24	2.20 ± 0.10	3.04
6.31	2.28 ± 0.07	5.88	1.25 ± 0.08	65–35	10.0	3.12 ± 0.15	3.12
8.32	3.10 ± 0.15	6.88	1.23 ± 0.07	70–30	16.6	4.78 ± 0.22	2.88
16.2	6.55 ± 0.19	10.2	1.23 ± 0.06	80–20	52.5	14.5 ± 0.77	2.76
30.9	12.9 ± 0.62						

[a] At 35 °C; [MPS] = 5.0 × 10⁻³ M; [Cr(VI)] = 5.0 × 10⁻⁴ M. [b] I = 0.320 M; solvent 50:50 AcOH-H₂O (v/v). [c] [HClO₄] = 1.0 × 10⁻³ M; solvent 50:50 AcOH-H₂O (v/v). [d] [HClO₄] = 1.0 × 10⁻³ M.

Table III. Second-Order Rate Constants and Enthalpies and Entropies of Activation for the Oxidation of XC₆H₄SMe by Cr(VI)[a]

no.	X	10^3k_2, M⁻¹ s⁻¹			$\Delta H^{\ddagger}$,[b] kJ mol⁻¹	$-\Delta S^{\ddagger}$,[b] J K⁻¹ mol⁻¹
		30 °C	40 °C	50 °C		
1	H	20.9 ± 0.81	31.1 ± 0.74	42.3 ± 1.8	25.9 ± 2.8	192 ± 9.6
2	p-MeO	116 ± 13	199 ± 16	312 ± 19	37.6 ± 6.7	139 ± 23
3	p-Me	40.8 ± 2.2	58.5 ± 2.9	82.3 ± 4.8	26.1 ± 4.4	186 ± 15
4	p-i-Pr	36.7 ± 1.5	52.5 ± 1.9	76.5 ± 4.2	27.4 ± 3.6	183 ± 12
5	m-Me	23.4 ± 1.3	33.3 ± 1.6	48.4 ± 2.3	27.1 ± 4.1	187 ± 14
6	p-F	17.5 ± 0.59	25.6 ± 1.3	36.9 ± 1.2	27.9 ± 3.2	187 ± 11
7	m-MeO	15.1 ± 0.62	21.5 ± 1.0	32.1 ± 1.0	28.2 ± 3.3	187 ± 11
8	p-Cl	9.81 ± 0.44	14.1 ± 0.69	20.5 ± 0.90	27.4 ± 3.7	193 ± 13
9	p-Br	8.80 ± 0.32	12.9 ± 0.42	18.5 ± 0.71	27.7 ± 2.9	193 ± 9.9
10	m-Cl	4.66 ± 0.21	6.68 ± 0.23	9.21 ± 0.46	25.2 ± 3.5	207 ± 12
11	p-COOH	2.08 ± 0.14	2.98 ± 0.19	4.32 ± 0.12	27.1 ± 4.2	207 ± 14
12	p-COCH₃	1.97 ± 0.05	3.00 ± 0.10	4.33 ± 0.14	29.5 ± 2.4	200 ± 8.3
13	p-NO₂	0.512 ± 0.03	0.684 ± 0.10	0.887 ± 0.04	19.8 ± 6.7	243 ± 23

[a] General conditions: [Cr(VI)] = 5.0 × 10⁻⁴ M; [HClO₄] = 1.0 × 10⁻³ M; I = 5.88 × 10⁻² M; solvent 50:50 AcOH-H₂O (v/v). [b] The precision of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values were calculated by using the method of Petersen et al.[20]

tween $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is valid,[19] a plot of $\Delta H^{\ddagger}$ against $\Delta S^{\ddagger}$ gives only a fair correlation (r = 0.911, s = 1.7). However, an excellent correlation is obtained when log k_{T_2} (50 °C) is plotted against log k_{T_1} (30 °C), (b = 1.04, r = 0.999, s = 0.03). The isokinetic temperature[21] has been found to be 119 K. According to Bunnett[22] if the experimental temperature is above the isokinetic temperature in a reaction series obeying a isokinetic relationship, then the reaction of highest entropy has the highest rate. Our results here are also in accordance with this postulate (cf. Table III). The excellent correlation between log k_{T_1} and log k_{T_2} suggests that the reaction under investigation follows a common mechanism. Since the isokinetic relationship is applicable to the data, Hammett correlation (Figure 1) of log k_2 with σ has been attempted (ρ = -2.07 ± 0.20, r = 0.989, s = 0.10 at 30 °C; ρ = -2.11 ± 0.23, r = 0.987, s = 0.11 at 40 °C; ρ = -2.15 ± 0.25, r = 0.985, s = 0.12 at 50 °C). It is seen that the magnitude of the ρ value is not too high. CNDO/2 calculations[23] show that the HOMO of methyl phenyl sulfide is mostly heteroatom lone pair in nature (with $\simeq$ 75% sulfur lone pair) and the HOMO in its para derivatives is formed by nonbonding combination of the sulfur 3p and the appropriate ring and substituent π orbitals with the prevailing contribution from the sulfur lone pair; it is therefore reasonable to correlate
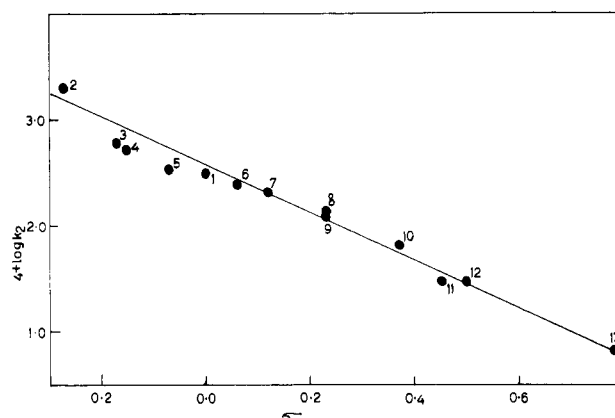

Figure 1. Hammett plot for substituted phenyl methyl sulfides at 40 °C. The points in the figure are referred to by the same numbers as the substituents in Table III.

the first ionization energies of para-substituted phenyl methyl sulfides (obtained from PES[23]) with our rate data to know whether the oxidation proceeds through a one-electron-transfer process. An excellent correlation is obtained when log k_2 is plotted against first ionization energies (r = 0.994), giving the expected negative slope. We find a good correlation (r = 0.990) between log k_2 and oxidation potential of sulfides. Such a good correlations has been taken as kinetic evidence for the one-electron-transfer process in enzyme oxygenation of aryl methyl sulfides.[24,25] Thus the excellent correlations of log k_2 with ionization energies as well as with oxidation potentials and the low value of ρ presumably point out one-electron transfer in the Cr(VI) oxidation of aryl methyl sulfides.

(19) The method of error analysis by Petersen et al. and Wiberg[20] has been applied to $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ data. For a valid relationship between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, the range of observed $\Delta H^{\ddagger}$ ($\Delta \Delta H^{\ddagger}$) must exceed 2δ (δ, the maximum possible error). Since $\Delta \Delta H^{\ddagger}$ (17.8 kJ mol⁻¹) is > 2δ (13 kJ mol⁻¹) in the present study, the correlation between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is significant.

(20) Petersen, R. C.; Markgraf, J. H.; Ross, S. D. *J. Am. Chem. Soc.* **1961**, *83*, 3819. Wiberg, K. B. "Physical Organic Chemistry"; Wiley: New York, 1964; p 376.

(21) Exner, O. *Nature (London)* **1964**, *201*, 488; *Collect. Czech. Chem. Commun.* **1964**, *29*, 1094.

(22) Bunnett, J. F. In "Investigation of Rates and Mechanism of Reactions – Techniques of Chemistry"; Lewis, E. S., Ed.; John-Wiley and Sons: New York, 1974; Vol. 6, p 413, 417.

(23) Bernardi, F.; Distefano, G.; Mangini, A.; Pignataro, S.; Sounta, S. *J. Electron Spectrosc. Relat. Phenom.* **1975**, *7*, 457.

(24) Watanabe, Y.; Iyanagi, T.; Oae, S. *Tetrahedron Lett.* **1980**, *21*, 3685.

(25) Watanabe, Y.; Numata, T.; Iyanagi, T.; Oae, S. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1163. (a) Sullivan, P. P.; Shine, H. J. *J. Phys. Chem.* **1971**, *75*, 411. Shine, H. J.; Rahman, M.; Seeger, H.; Wu, G. S. *J. Org. Chem.* **1967**, *32*, 190.

Table IV. Second-Order Rate Constants for the Oxidation of Alkyl Phenyl Sulfides with Cr(VI) at 40 °C and Relative Rates of Oxidation[a]
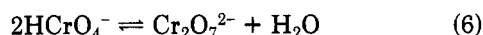
sulfide	$10^3 k_2$, M^{-1} s^{-1}	relative rates of oxidation			
		Cr(VI)	PIA[b]	$P_2O_8^{4-c}$	$S_2O_8^{2-d}$
PhSMe	31.1 ± 0.74	100	100	100	100
PhSEt	24.7 ± 1.4	80	88	66	41
PhS-n-Pr	23.5 ± 1.1	76	80	56	31
PhS-i-Pr	14.6 ± 0.66	47	72	32	15
PhS-t-Bu	3.33 ± 0.17	11	42	6.0	1.8

[a] General reaction conditions: [Cr(VI)] = 5.0 × 10^{-4} M; [HClO$_4$] = 1.0 × 10^{-3} M; I = 5.88 × 10^{-2} M; solvent 50:50 AcOH–H$_2$O (v/v). [b] Values from ref 7. [c] Values from ref 3. [d] Values from ref 2d.

Scheme I
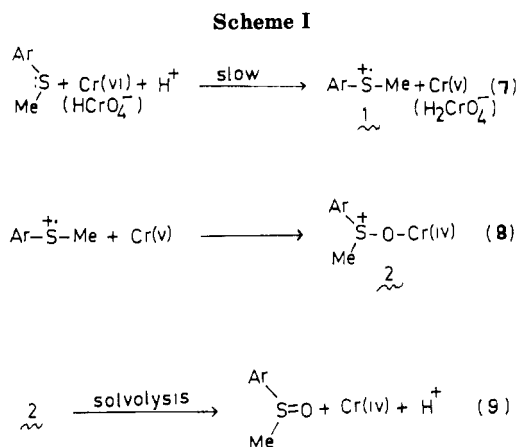
In certain cases the formation of cation radicals from aromatic sulfides has been firmly established in recent years.[25a]

(B) Mechanism of Oxidation. In aqueous solutions of Cr(VI) at concentrations greater than 0.05 M, the dichromate ion and its protonated forms are the predominant species. At dilute solution (as in the present case) the monomeric form predominates.[26] The acid chromate

$$H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^- \quad (4)$$

$$HCrO_4^- \rightleftharpoons H^+ + CrO_4^{2-} \quad (5)$$

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O \quad (6)$$

ion HCrO$_4^-$ does not lose a proton until the pH is raised to about 7 and it gains a second proton in the H$_-$ range of -1 to -3. At higher concentrations of HClO$_4$, Cr(VI) mainly exists as HCrO$_3^{+}$.[27,28] In the present investigation the acid concentration is very low and under this condition the active oxidizing species is HCrO$_4^-$.[17] On the basis of the foregoing arguments based on kinetic data, a mechanism involving a one-electron-transfer process (Scheme I) is proposed for the oxidation of MPS by Cr(VI). The solvolysis step (eq 9) is not likely to be the rate-determining step as it requires a positive ρ value. A similar type of mechanism has been proposed by Wiberg and Lepse[29] in the oxidation of diphenyl sulfide by diacetyl chromate. The mechanism accounts for the observed rate law (eq 3). A two-electron-transfer process will result in the formation of Cr(IV), which can be demonstrated by the addition of Mn(II).[28] The addition will generally lead to a decreased rate of oxidation because Mn(II) removes the Cr(IV) formed. The rate of oxidation of MPS by Cr(VI) is almost unaffected by the addition of Mn(II), ruling out the pos-

Table V. Pseudo-First-Order and Second-Order Rate Constants for the Reaction of DPS with Cr(VI) in 75:25 AcOH–H$_2$O (v/v)[a]

10^2[DPS], M	10^3[Cr(VI)], M	$10^4 k_1$, s^{-1}	$10^2 k_2$, M^{-1} s^{-1}
0.500[b]	0.500	1.04 ± 0.03	2.08 ± 0.06
0.600[b]	0.500	1.19 ± 0.03	1.98 ± 0.03
0.800[b]	0.500	1.58 ± 0.10	1.97 ± 0.13
0.800	0.250[c]	1.52 ± 0.12	1.91 ± 0.14
0.800	0.750[c]	1.45 ± 0.05	1.81 ± 0.07

[a] At 30 °C; [HClO$_4$] = 2.0 × 10^{-2} M. [b] I = 3.15 × 10^{-1} M. [c] I = 3.50 × 10^{-1} M.

sibility of the formation of Cr(IV) in the rate-controlling step, eq 7.

(C) Steric Effects in the Oxidation of Alkyl Phenyl Sulfides. As observed in the oxidation of alkyl phenyl sulfides PhSR (R = Me, Et, n-Pr, i-Pr, t-Bu) by peroxyanions[2d,3] and (diacetoxyiodo)benzene,[7] Cr(VI) oxidation of these sulfides also show the same order of rate decrease, viz., PhSMe > PhSEt > PhS-n-Pr > PhS-i-Pr > PhS-t-Bu (Table IV). If the inductive effect of the alkyl groups predominate, then the reverse order of reactivity should have been observed. Further, satisfacotry correlation is obtained when log (k_2/k_2Me) is plotted against E_s, the Taft's steric substituent constant (slope = 0.625 ± 0.18, r = 0.988, s = 0.07). These facts establish that the reaction is sensitive to steric crowding at the reaction center, sulfur.

(D) Oxidation of Diphenyl Sulfides. There are only a few studies on the effect of substituent in the oxidation of diphenyl sulfides. They cover the oxidation by H$_2$O$_2$,[5] photooxygenation,[30] and by (diacetoxyiodo)benzene.[31] Recently we were struck by certain interesting observations encountered during our kinetic studies on the oxidation of organic sulfur compounds: (i) while the oxidations of aryl methyl sulfides by peroxydisulfate[2a,d] and peroxydiphosphate[3] ions are second order, the oxidation of diphenyl sulfide by these peroxyanions[2e] follows first-order kinetics in peroxyanion and zero order in the sulfide and (ii) in contrast, the oxidation of aryl methyl sulfides[7] and diphenyl sulfides[31] by (diacetoxyiodo)benzene follows second-order kinetics. It was, therefore, considered of interest to extend our studies to diphenyl sulfides. The rates of oxidation of diphenyl sulfides by Cr(VI) were first tried under the same conditions as employed for aryl methyl sulfides, but the reactions were too slow to follow at convenient rates. Hence the oxidations have been carried out in a 75:25 acetic acid–water (v/v) mixture. Detailed studies with diphenyl sulfide (DPS) indicate that the order with respect to each of Cr(VI) and DPS is unity as indicated by the linearity of the plot of log ($a - k$) vs. time, constant pseudo-first-order rate constants at different initial [Cr(VI)], and the constant k_2 values at different initial [DPS] (Table V). Rate studies at three temperatures with 4-

(26) Wiberg, K. B., Ed. "Oxidation in Organic Chemistry"; Academic Press: New York, 1965; p 71, 182.
(27) Levitt, L. S. *J. Org. Chem.* 1955, 20, 1297.
(28) Graham, G. T. E.; Westheimer, F. H. *J. Am. Chem. Soc.* 1958, 80, 3030.
(29) Wiberg, K. B.; Lepse, P. A. *J. Am. Chem. Soc.* 1964, 86, 2612.

(30) Ando, W.; Kabe, Y.; Miyazaki, H. *Photochem. Photobiol.* 1980, 31, 191.
(31) Srinivasan, C.; Chellamani, A. *Indian J. Chem.* 1983, 22B, 173.

Table VI. Second-Order Rate Constants and Enthalpies and Entropies of Activation for the Oxidation of XC₆H₄SPh by Cr(VI)[a]

		$10^3 k_2$, M^{-1} s^{-1}				
no.	X	30 °C	40 °C	50 °C	ΔH^*, kJ mol^{-1}	$-\Delta S^*$, J K^{-1} mol^{-1}
1	H	20.1 ± 0.08	35.0 ± 1.0	60.0 ± 2.2	42.0 ± 2.9	139 ± 9.7
2	4-MeO	46.0 ± 2.5	77.2 ± 3.1	132 ± 9.0	40.5 ● 4.4	137 ± 15
3	4-Me	41.7 ± 1.7	69.1 ± 2.8	118 ± 5.0	39.7 ± 3.4	141 ± 11
4	4-Cl	9.17 ± 0.40	14.7 ± 1.2	24.8 ± 1.6	38.0 ± 5.1	159 ± 18
5	4-Br	7.87 ± 0.37	13.9 ± 0.40	24.7 ± 0.90	44.0 ± 3.0	140 ± 10
6	4-NO₂	0.653 ± 0.05	1.10 ± 0.11	2.19 ± 0.09	46.6 ± 6.0	153 ± 21

[a] General conditions: [Cr(VI)] = 5.0 × 10^{-4} M; [HClO₄] = 2.0 × 10^{-2} M; I = 3.15 × 10^{-2} M; solvent 75:25 AcOH–H₂O (v/v).

substituted diphenyl sulfides show that electron-releasing substituents accelerate the rate of oxidation (Table VI). Excellent correlation exists between log k_2 and σ and the ρ value is small (ρ = -1.80 ± 0.27, r = 0.994, s = 0.08 at 30 °C; ρ = -1.80 ± 0.26, r = 0.995, s = 0.08 at 40 °C; ρ = -1.74 ± 0.22, r = 0.996, s = 0.07 at 50 °C). The active oxidizing species under the conditions employed is HCrO₄$^-$ and the oxidation of diphenyl sulfides is likely to follow the one-electron-transfer process as suggested for alkyl aryl sulfides. For this series of reactions the $\Delta H^* - \Delta S^*$ relationship is not valid since the Petersen's[19] error criteria is not satisfied ($\Delta\Delta H^*$ = 8.60 kJ mol^{-1}, δ = 6.0 kJ mol^{-1}). However, correlation with Exner's equation[21] is excellent (b = 0.964, r = 0.999, s = 0.02).

Experimental Section

Materials. All the alkyl aryl sulfides were prepared by known methods.[2,32] Diphenyl sulfide, 4-methoxydiphenyl, 4-methyldiphenyl, 4-chlorodiphenyl- and 4-bromodiphenyl sulfides were obtained from the corresponding thiophenol and iodobenzene.[33] From the reaction of 4-chloronitrobenzene and sodium thiophenolate, 4-nitrodiphenyl sulfide was prepared.[34] The sulfides were purified by vacuum distillation/recrystallization from suitable solvents. The boiling point, melting point, n^{30}D, and d^{30}_4 of these sulfides were found to be identical with literature values.[32,35] Further, the sulfides show no impurity peaks in the ¹H NMR spectra, and the TLC analyses proved the presence of a single entity in each sulfide.

Potassium dichromate (BDH, AR), sodium perchlorate (GR, E. Merck) and 60% perchloric acid (GR, E. Merck) were used as such. Acetic acid was purified by refluxing with chromium trioxide, as described by Orton and Bradfield.[36] To evaluate the hydrogen ion concentration, the pH of the solutions were measured with a digital pH meter, Model pH 5651 of Electronic Corporation of India Ltd.

Kinetic Measurements. The kinetic studies were carried out in 50:50 acetic acid–water (v/v) and in the 75:25 acetic acid–water (v/v) mixtures in the case of alkyl aryl sulfides and diphenyl sulfides, respectively, under pseudo-first-order conditions and the temperature was maintained within ±0.1 °C. The titrimetric procedure of Wiberg and Mill[17] was followed for the estimation of unreacted Cr(VI). A stock solution of 0.05 M potassium di-

chromate was freshly prepared prior to the kinetic run and the appropriate quantity of this solution was mixed with the reaction mixture so as to get the required concentration of Cr(VI). The pseudo-first-order rate constant (k_1) for each run was evaluated from the slope of the linear plot of log ($a - x$) vs. time by the method of least-squares using a Micro 2200 diskette recorder (Hindustan Computers Limited). Reproducible results giving good first-order plots, correlation coefficient r > 0.995, were obtained for reactions run in duplicate/triplicate, in each substrate and at all temperatures studied. The second-order rate constants were obtained from $k_2 = k_1/$[sulfide]. The precision of the k values is given in terms of 95% confidence limits of the Student's t test.[3] The kinetic data fit the Arrhenius equation and the activation parameters were obtained by the method of least squares. The errors in activation parameters were calculated by the method of Petersen et al.[20]

Product Analysis. The reaction mixture from an actual kinetic run in the oxidation of methyl phenyl sulfide was extracted with ether and dried over anhydrous sodium sulfate, and the solvent was removed. The residue was analyzed by TLC (silica gel) using an 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, indicating that under the experimental conditions sulfide is oxidized to the sulfoxide stage only. This is also confirmed by the fact that there was no oxidation of methyl phenyl sulfoxide under identical kinetic conditions as employed for the sulfide.

Stoichiometry. Estimation of the unreacted Cr(VI) from reaction mixtures where [Cr(VI)] > [sulfide] after the completion of the reaction showed that three molecules of sulfide are oxidized for each two Cr(VI) species reduced to Cr(III). The stoichiometry is represented by
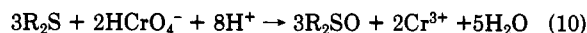
$$3R_2S + 2HCrO_4^- + 8H^+ \rightarrow 3R_2SO + 2Cr^{3+} + 5H_2O \quad (10)$$

Registry No. HCrO₄$^-$, 15596-54-0; PhSMe, 100-68-5; *p*-MeOC₆H₄SMe, 1879-16-9; *p*-MeC₆H₄SMe, 623-13-2; *p*-(*i*-Pr)C₆H₄SMe, 70026-35-6; *m*-MeC₆H₄SMe, 4886-77-5; *p*-FC₆H₄SMe, 371-15-3; *m*-MeOC₆H₄SMe, 2388-74-1; *p*-ClC₆H₄SMe, 123-09-1; *p*-BrC₆H₄SMe, 104-95-0; *m*-ClC₆H₄SMe, 4867-37-2; *p*-(COOH)C₆H₄SMe, 13205-48-6; *p*-(COCH₃)C₆H₄SMe, 1778-09-2; *p*-NO₂C₆H₄SMe, 701-57-5; PhSEt, 622-38-8; PhS-*n*-Pr, 874-79-3; PhS-*i*-Pr, 3019-20-3; PhS-*t*-Bu, 3019-19-0; PhSPH, 139-66-2; 4-MeOC₆H₄SPh, 5633-57-8; 4-MeC₆H₄SPh, 3699-01-2; 4-ClC₆H₄SPh, 13343-26-5; 4-BrC₆H₄SPh, 65662-88-6; 4-NO₂C₆H₄SPh, 952-97-6; potassium dichromate, 7778-50-9.

(32) Baliah, V.; Uma, M. *Tetrahedron* **1963**, *19*, 455.
(33) Mauthner, F. *Chem. Ber.* **1906**, *39*, 3594.
(34) Hodgson, H. H.; Smith, R. *J. Chem. Soc.* **1937**, 1634.
(35) *Chem. Abstr.* **1954**, *48*, 1303. Pollock, J. R. A., Stevens, R., Eds. "Dictionary of Organic Compounds"; Eyre and Spottiswoode: London, 1965; Vol. 1, p 482. Sanesi, M.; Leandri, G. *Ann. Chim. (Rome)* **1955**, *45*, 1106.
(36) Orton, K. J. P.; Bradfield, A. E. *J. Chem. Soc.* **1926**, 986.