

Separation of electronic and steric effects: Oxidation of *ortho*-substituted phenyl methyl sulphides by peroxyanions, chromium(VI) and picolinic acid catalysed chromium(VI)

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Abstract. The kinetics of oxidation of *ortho*-substituted phenyl methyl sulphides by peroxyanions, Cr(VI) and picolinic acid catalysed Cr(VI) have been investigated. Regression analyses of the rate data by using Taft and Charton equations to separate steric effect from electronic effects have been carried out. In peroxyanion oxidations, the localized electronic effect plays a major role. In the uncatalysed and picolinic acid catalysed Cr(VI) oxidations, both localized and delocalized effects are significant. Steric effect plays a minor role in all the oxidations.

Keywords. *ortho*-substituted phenyl methyl sulphides; *ortho*-effect; regression analysis.

1. Introduction

The kinetics of oxidation of alkyl aryl sulphides with peroxydisulphate (PS) (Arumugam *et al* 1978; Srinivasan *et al* 1978), peroxydiphosphate (PP) (Srinivasan *et al* 1980) and uncatalysed and picolinic acid (PA) catalysed Cr(VI) (Srinivasan *et al* 1982) have been extensively investigated in this laboratory. The mechanisms of these oxidations have been established based on the kinetic results obtained with several *para*- and *meta*-substituted phenyl methyl sulphides and from a comprehensive analysis of the rate constants employing linear free-energy relationships. A polar mechanism has been proposed for the oxidation of alkyl aryl sulphides by peroxyanions. On the other hand a mechanism involving one-electron transfer process is envisaged in the uncatalysed and PA catalysed Cr(VI) oxidations. Rates of oxidation of several alkyl phenyl sulphides with the above oxidants also reveal that the reaction centre *viz* the sulphide sulphur is quite sensitive to steric congestion. These studies prompted us to investigate the influence of *ortho*-substituents in the oxidation of aryl methyl sulphides. *Ortho*-substituted benzene derivatives often behave differently from the corresponding *meta*- or *para*-substituted compounds. This peculiarity of *ortho*-substituted compounds is sometimes named *ortho*-effect. Numerous attempts (Taft 1956; Charton 1971, 1975; Fujita and Nishioka 1976) have been made to understand quantitatively the nature and composition of the *ortho*-effect, by separating the component effects from each other. The present work is part of an effort to develop a better understanding of the *ortho*-effect in these oxidations. The kinetic data are analysed by employing Taft and Charton treatments.

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2. Experimental

All the *ortho*-substituted phenyl methyl sulphides were obtained by the methylation of the corresponding thiols which were obtained from the *ortho*-substituted anilines by the xanthogenic ester method (Horning 1955). The kinetic measurements were carried out under pseudo first-order conditions by estimating the unreacted oxidant using iodometric procedure. The reaction conditions were identical with those employed in the kinetic studies of *meta*- and *para*-substituted phenyl methyl sulphides (Arumugam *et al* 1978; Srinivasan *et al* 1980, 1982). Statistical calculations were performed with a Micro 2200 diskette recorder (Hindustan Computers). The rate constants were measured at three temperatures. The rate data at 40°C are considered for the analysis of the *ortho*-effect. The substituent parameters are taken from literature (Taft 1956; Shorter 1972; Aslam *et al* 1981).

3. Results and discussion

3.1 Oxidation of *ortho*-substituted phenyl methyl sulphides by peroxyanions

The oxidation of *ortho*-substituted phenyl methyl sulphides by PS was carried out in 50% (v/v) aqueous ethanol while that by PP in 50% (v/v) aqueous acetic acid. The rate data and the activation parameters are set forth in tables 1 and 2. The data reveal that the reactivity is in the order H > Me > OMe > F > Cl > Br > NO₂. Regression analyses have been carried out with Taft's linear free-energy—polar energy relationship [equation (1)] and linear free energy—steric energy relationship [equation (2)] (Taft 1956).

$$\log k_{\text{ortho}} = \rho^* \sigma_0^* + h \quad (1)$$

$$\log k_{\text{ortho}} = \delta E_s + h \quad (2)$$

In the above equations, σ_0^* (polar) and E_s (steric) are the substituent constants, ρ^* is a

Table 1. Second-order rate constants, enthalpies and entropies of activation for the oxidation of *ortho*-substituted phenyl methyl sulphides by PS^a.

Substituent	10 ³ k ₂ M ⁻¹ sec ⁻¹ ^b			ΔH ^{‡c} (kJ mol ⁻¹)	-ΔS ^{‡c} (JK ⁻¹ mol ⁻¹)
	35°	40°	45°		
H	4.41 ± 0.18	5.90 ± 0.15	7.87 ± 0.39	44.8 ± 6.3	146 ± 21
Me	3.65 ± 0.13	5.07 ± 0.25	6.64 ± 0.11	46.5 ± 5.4	141 ± 18
MeO	2.03 ± 0.06	2.85 ± 0.05	3.77 ± 0.13	47.7 ± 4.6	142 ± 15
F	0.821 ± 0.01	1.15 ± 0.03	1.57 ± 0.03	50.2 ± 3.4	142 ± 11
Cl	0.620 ± 0.03	0.860 ± 0.02	1.25 ± 0.05	54.4 ± 6.3	130 ± 21
Br	0.493 ± 0.01	0.611 ± 0.02	0.856 ± 0.04	61.1 ± 5.9	113 ± 19
NO ₂	—	0.324 ± 0.04	0.447 ± 0.02	50.7 ± 28	150 ± 88

^aGeneral conditions: [Sulphide] ≈ 0.02 M; [S₂O₈²⁻] = 0.001 M in 50% (v/v) aqueous ethanol at I = 0.015 M

^bThe error quoted in k₂ is 95% CL of the 'Student *t*'

^cThe precision of ΔH[‡] and ΔS[‡] values were calculated using the method of Petersen *et al* (1961).

Table 2. Second-order rate constants, enthalpies and entropies of activation for the oxidation of *ortho*-substituted phenyl methyl sulphides by PP^a.

Substituent	10 ³ k ₂ M ⁻¹ s ⁻¹			ΔH [‡] (kJ mol ⁻¹)	-ΔS [‡] (JK ⁻¹ mol ⁻¹)
	35°	40°	45°		
H	6.67 ± 0.32	9.90 ± 0.44	14.2 ± 0.67	59.9 ± 7.5	92.9 ± 25
Me	4.96 ± 0.44	7.59 ± 0.37	11.2 ± 0.09	63.6 ± 8.0	82.5 ± 26
MeO	4.32 ± 0.59	5.81 ± 0.42	8.16 ± 0.52	49.4 ± 15	131 ± 46
F	1.32 ± 0.09	2.03 ± 0.14	3.25 ± 0.16	70.7 ± 10	70.7 ± 34
Cl	0.918 ± 0.10	1.51 ± 0.13	2.58 ± 0.14	81.6 ± 14	38.9 ± 42
Br	0.813 ± 0.04	1.31 ± 0.08	2.15 ± 0.11	75.3 ± 8.8	59.9 ± 29
NO ₂	0.453 ± 0.03	0.764 ± 0.05	1.26 ± 0.11	80.8 ± 12	46.9 ± 39

^aGeneral conditions: [Sulphide] ≈ 0.02 M; [PP] = 0.001 M in 50% (v/v) aqueous acetic acid at I = 0.2 M and [H⁺]_T = 0.0138 M.

reaction constant analogous to ρ and δ is a steric susceptibility constant. The results of the regression analyses with the Taft's relationships are expressed by the following equations

PS oxidation

$$\log k_{\text{ortho}} = -0.962 \sigma_0^* - 2.618$$

$$r = 0.893; s = 0.22; n = 6$$

(r = correlation coefficient; s = standard deviation; n = number of data points)

$$\log k_{\text{ortho}} = 0.457 E_s - 2.994$$

$$r = 0.604; s = 0.39; n = 6$$

PP oxidation

$$\log k_{\text{ortho}} = -0.871 \sigma_0^* - 2.368$$

$$r = 0.913; s = 0.18; n = 6$$

$$\log k_{\text{ortho}} = 0.419 E_s - 2.709$$

$$r = 0.625; s = 0.34; n = 6$$

For these oxidations a fair correlation with (1) and a poor correlation with (2) indicate the minor role of the 'primary steric effect' or the 'bulk effect'.

To understand the composition of localized (L), delocalized (D) and steric components (S) operating in these reactions, the rate data are analysed with LD (Taft and Lewis 1958) and LDS (Charton *et al* 1979) equations ((3) and (4)).

$$\log k_{\text{ortho}} = L\sigma_I + D\sigma_R + h \quad (3)$$

$$\log k_{\text{ortho}} = L\sigma_I + D\sigma_R + Sv + h \quad (4)$$

where σ_I, σ_R and v are inductive, resonance and steric substituent constants respectively. The v scale has been developed by Charton (Charton and Charton 1978; Aslam *et al* 1981) based on the consideration of van der Waals' radii and Taft's E_s values. The results of the correlation are given below:

ps oxidation

$$\log k_{\text{ortho}} = -1.75 \sigma_I - 0.459 \sigma_R - 2.322$$

$$(\pm 0.194) \quad (\pm 0.210)$$

$$R = 0.977; \text{SE} = 0.126; n = 7 \text{ (unsubstituted compound included);}$$

$$\text{CL} = 97.5\%$$

(R = multiple correlation coefficient; SE = standard error of the estimate; n = number of data points; CL = confidence level of F test significance)

$$\log k_{\text{ortho}} = -1.59 \sigma_I - 0.576 \sigma_R - 2.434$$

$$(\pm 0.243) \quad (\pm 0.228)$$

$$R = 0.977; \text{SE} = 0.121; n = 6 \text{ (unsubstituted compound excluded); CL} = 97.5\%$$

$$\log k_{\text{ortho}} = -1.58 \sigma_I - 0.318 \sigma_R - 0.156 \nu - 2.267$$

$$(\pm 0.317) \quad (\pm 0.296) \quad (\pm 0.216)$$

$$R = 0.980; \text{SE} = 0.134; n = 7; \text{CL} = 99\%$$

pp oxidation

$$\log k_{\text{ortho}} = -1.56 \sigma_I - 0.419 \sigma_R - 2.108$$

$$(\pm 0.199) \quad (\pm 0.215)$$

$$R = 0.970; \text{SE} = 0.129; n = 7; \text{CL} = 97.5\%$$

$$\log k_{\text{ortho}} = -1.38 \sigma_I - 0.550 \sigma_R - 2.234$$

$$(\pm 0.230) \quad (\pm 0.223)$$

$$R = 0.972; \text{SE} = 0.119; n = 6; \text{CL} = 95\%$$

$$\log k_{\text{ortho}} = -1.45 \sigma_I - 0.330 \sigma_R - 0.097 \nu - 2.073$$

$$(\pm 0.342) \quad (\pm 0.320) \quad (\pm 0.233)$$

$$R = 0.971; \text{SE} = 0.144; n = 7; \text{CL} = 97.5\%$$

Correlations obtained with LD and LDS equations are justified by F -test significance ($> 95\%$ CL). For oxidations with peroxyanions the L and D terms in LD equations are significant to $> 99.8\%$ and 90% CL (t -test) respectively when the unsubstituted compound is included in the regression analyses. On excluding the unsubstituted compound the L term is significant to 99.5% and 99% CL of the t -test in ps and pp oxidations respectively; the D term is significant to 90% CL in both oxidations. These analyses undoubtedly indicate that the localised effect plays a major role in these oxidations. A better description of the composition of the electrical effect is given by the 'percent delocalized factor', P_D , where $P_D = D \times 100 / L + D$ (Charton 1975). The P_D values are 26.6 and 20.8 for excluding and including the unsubstituted compound for the ps oxidation and the corresponding values are 28.5 and 21.2 for the pp oxidation. The h_{obs} value (-3.229) is not very close to the h_{cal} (-2.434 , unsubstituted excluded; -2.322 , unsubstituted included) for ps oxidation. Similar behaviour is also noted with pp oxidation ($h_{\text{obs}} = -3.002$; $h_{\text{cal}} = -2.234$ (unsubstituted excluded) and -2.108 (unsubstituted included)).

In analysing with LDS equation, the L and D terms are significant to 98% and 50% CL

of *t*-test respectively in both oxidations and the *S* term is significant to 50% and < 50% CL in PS and PP oxidations respectively. These results also clearly demonstrate the operation of significant localised effect and insignificant delocalised and steric effects in the peroxyanion oxidations. These results indicate that these reaction series may be taken as examples of case 3 of Charton's classification ($\log k_{\text{ortho}} = L\sigma_I + D\sigma_R + h'$; $h' \neq h$; Charton 1975).

3.2 Oxidation of ortho-substituted phenyl methyl sulphides by Cr(VI) and PA catalysed Cr(VI)

PA is a specific catalyst for the Cr(VI) oxidation of alcohols (Rocek and Peng 1977). Recently we have observed that PA accelerates the Cr(VI) oxidation of alkyl aryl and diphenyl sulphides and the rate acceleration has been attributed to the fast attack of PA complexed Cr(VI) on the sulphide (Srinivasan *et al* 1982). Hence we have measured the rates of both uncatalysed and PA catalysed Cr(VI) oxidations of *ortho*-substituted phenyl methyl sulphides in 50% (v/v) aqueous acetic acid. The kinetic data presented in tables 3 and 4 show that the order of reactivity is H > OMe > Me > F > Br > Cl > NO₂. Correlation analyses have been carried out with equations (1) and (2). The

Table 3. Second-order rate constants, enthalpies and entropies of activation for the oxidation of *ortho*-substituted phenyl methyl sulphides by Cr(VI)^a.

Substituent	$10^3 k_2 \text{ M}^{-1} \text{ s}^{-1}$			ΔH^\ddagger (kJ mol ⁻¹)	$-\Delta S^\ddagger$ (JK ⁻¹ mol ⁻¹)
	30°	40°	50°		
H	20.9 ± 0.81	31.1 ± 0.74	42.3 ± 1.8	25.9 ± 2.8	192 ± 9.6
MeO	17.4 ± 0.68	25.9 ± 0.42	37.3 ± 1.0	28.5 ± 2.2	185 ± 7.6
Me	17.2 ± 0.48	25.1 ± 0.97	25.6 ± 0.73	27.1 ± 2.4	190 ± 8.2
F	2.10 ± 0.04	2.98 ± 0.19	4.45 ± 0.20	27.9 ± 3.5	204 ± 12
Br	1.61 ± 0.07	2.44 ± 0.05	3.49 ± 0.22	28.9 ± 3.5	203 ± 12
Cl	0.875 ± 0.09	1.28 ± 0.12	2.00 ± 0.06	31.3 ± 6.0	201 ± 21
NO ₂	0.114 ± 0.02	0.173 ± 0.04	0.228 ± 0.02	25.9 ± 13	235 ± 44

^aGeneral conditions: [Sulphide] ≈ 0.01 M; [Cr(VI)] = 0.0005 M in 50% (v/v) aqueous acetic acid at *l* = 0.02 M and [HClO₄] = 0.001 M.

Table 4. Second-order rate constants, enthalpies and entropies of activation for the PA catalysed Cr(VI) oxidation of *ortho*-substituted phenyl methyl sulphides^a.

Substituent	$10^2 k_2 \text{ M}^{-1} \text{ s}^{-1}$			ΔH^\ddagger (kJ mol ⁻¹)	$-\Delta S^\ddagger$ (JK ⁻¹ mol ⁻¹)
	30°	40°	50°		
H	19.4 ± 1.4	27.1 ± 1.0	30.1 ± 3.5	15.4 ± 6.3	208 ± 21
MeO	18.4 ± 3.1	23.2 ± 4.2	27.4 ± 3.8	13.6 ± 13	214 ± 45
Me	17.2 ± 1.8	21.2 ± 3.4	26.1 ± 3.4	14.4 ± 11	212 ± 36
F	2.54 ± 0.43	3.98 ± 0.49	5.23 ± 0.62	26.9 ± 11	186 ± 38
Br	2.07 ± 0.29	3.43 ± 0.69	4.99 ± 0.76	33.3 ± 13	168 ± 46
Cl	1.13 ± 0.13	1.78 ± 0.29	2.53 ± 0.23	30.3 ± 10	182 ± 34
NO ₂	0.218 ± 0.02	0.377 ± 0.04	0.544 ± 0.07	34.5 ± 8.9	181 ± 30

^aGeneral conditions: [Sulphide] ≈ 0.01 M; [Cr(VI)] = 0.0005 M in 50% (v/v) aqueous acetic acid at *l* = 0.02 M, [HClO₄] = 0.001 M and [PA] = 0.001 M.

results of the correlations are expressed in the following equations:

Uncatalysed oxidation

$$\log k_{\text{ortho}} = -1.96\sigma_0^* - 1.872$$

$$r = 0.969; s = 0.23; n = 6$$

$$\log k_{\text{ortho}} = 1.05 E_s - 2.656$$

$$r = 0.738; s = 0.62; n = 6$$

Catalysed oxidation

$$\log k_{\text{ortho}} = -1.60\sigma_0^* - 0.8790$$

$$r = 0.967; s = 0.19; n = 6$$

$$\log k_{\text{ortho}} = 0.867 E_s - 1.520$$

$$r = 0.743; s = 0.51; n = 6$$

The operation of significant polar effect with a very minor role of primary steric effect becomes evident from the observed satisfactory correlations with (1) and poor correlations with (2) in both uncatalysed and catalysed oxidations. The data have been further analysed by LD and LDS equations and the results are given below:

Uncatalysed oxidation

$$\log k_{\text{ortho}} = -2.93\sigma_I - 1.49\sigma_R - 1.681$$

$$(\pm 0.271) (\pm 0.294)$$

$$R = 0.985; SE = 0.175; n = 7; CL = 97.5\%$$

$$\log k_{\text{ortho}} = -2.63\sigma_I - 1.71\sigma_R - 1.890$$

$$(\pm 0.266) (\pm 0.259)$$

$$R = 0.992; SE = 0.138; n = 6; CL = 99\%$$

$$\log k_{\text{ortho}} = -2.69\sigma_I - 1.30\sigma_R - 0.210\nu - 1.616$$

$$(\pm 0.446) (\pm 0.416) (\pm 0.303)$$

$$R = 0.987; SE = 0.188; n = 7; CL = 99.5\%$$

Catalysed oxidation

$$\log k_{\text{ortho}} = -2.39\sigma_I - 1.23\sigma_R - 0.7257$$

$$(\pm 0.257) (\pm 0.279)$$

$$R = 0.980; SE = 0.167; n = 7; CL = 97.5\%$$

$$\log k_{\text{ortho}} = -2.12\sigma_I - 1.43\sigma_R - 0.9180$$

$$(\pm 0.262) (\pm 0.255)$$

$$R = 0.988; SE = 0.136; n = 6; CL = 97.5\%$$

$$\log k_{\text{ortho}} = -2.18\sigma_I - 1.06\sigma_R - 0.192\nu - 0.6577$$

$$(\pm 0.427) (\pm 0.400) (\pm 0.290)$$

$$R = 0.983; SE = 0.180; n = 7; CL = 99\%$$

Though a satisfactory correlation is obtained with LDS equation (F -test significance is $> 99\%$ in both oxidations), the steric term is significant to only $< 50\%$ CL of the t -test. Successful correlation is obtained with LD equation (F -test significance $> 97.5\%$ CL in both oxidations). The L and D terms are significant to $> 99.5\%$ and $> 99\%$ CL of the t -test in both oxidations respectively. The P_D values are 39.4 and 33.7 for excluding and including the unsubstituted compound for the uncatalysed oxidation and the corresponding values are 40.3 and 34.0 for the catalysed oxidation. The value of h_{obs} (-1.508) is not very close to the h_{cal} (-1.890 , unsubstituted excluded; -1.681 , unsubstituted included for uncatalysed oxidation). Similar behaviour is also noted with catalysed oxidation ($h_{\text{obs}} = -0.576$; $h_{\text{cal}} = -0.918$ (unsubstituted excluded) and -0.726 (unsubstituted included)). These results indicate that the reaction series may also belong to case 3 of Charton's classification.

3.3 Isokinetic relationships

The Petersen's error criterion (Petersen *et al* 1961) *i.e.* the observed range of ΔH^\ddagger value should be greater than 2δ (where δ is the calculated maximum possible error) must be satisfied for the validity of $\Delta H^\ddagger - \Delta S^\ddagger$ isokinetic relationship. Except in PP oxidation, in all the other reaction series this condition is not satisfied. However, Exner plots (plots of $\log k_{45^\circ}$ vs $\log k_{35^\circ}$ in peroxyanions and plots of $\log k_{50^\circ}$ vs $\log k_{30^\circ}$ in uncatalysed and PA catalysed Cr(VI) oxidations) are excellent ($r \geq 0.995$). The existence of such isokinetic relationships is an indication of the operation of the same mechanism (Leffler 1955) in all sulphides in each oxidation.

4. Conclusion

The following conclusions emerge from the foregoing analyses: (i) The localized effect is a major component in all oxidations. (ii) the steric effect plays a minor role and appears to be constant. (iii) With the LDS equations the regression coefficients of σ_I , σ_R and ν terms are all negative. The negative sign of electronic-effect terms, *viz* σ_I and σ_R , is readily explicable in terms of the reaction mechanism (Srinivasan *et al* 1978, 1980, 1982). The negative regression coefficient for the ν (steric) term corresponds to the reaction being subject to steric retardation by *ortho*-substituents. (iv) The intercept h obtained in each of the reaction series by the application of LD and LDS equation does not correspond closely to the $\log k$ value for the parent system. (v) All these four reaction series may hence be considered as examples of case 3 of Charton's classification (Charton 1975).

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