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Oxidation of Some *Ortho*-substituted Phenyl Methyl Sulphides with Quinolinium Fluorochromate in Acetonitrile Medium

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The kinetics of oxidation of some *ortho*-substituted phenyl methyl sulphides with quinolinium fluorochromate (QFC) has been investigated in acetonitrile medium. Regression analysis was done with Taft's linear free-energy polar-energy relationship and linear free-energy steric-energy relationship. Steric contribution to this reaction seems to be much less than the polar effect. Analysis of rate data with LD and LDS equations emphasizes that localized effect plays a predominant role in this oxidation.

INTRODUCTION

Although the Hammett equation and its various modified forms apply to a number of reactions of *meta*- and *para*- substituted benzene derivaties, they fail for *ortho*-substituted benzene derivatives. In *ortho*-substituted compounds, the substituents cause other effects in addition to the well known inductive and resonance effects. These additional effects are very often referred to as 'proximity effect' and have been reported in various studies.

In an attempt to explain these proximity effects, many hypotheses were proposed such as primary[1] and secondary steric effects[2–4]. intramolecular hydrogen bonding[5], field effects[6–13] and solvation influencing effects[14] as well as several less-understood ones such as pondral effect[15], London forces[16] and miserable effects[17]. The proximity effects for a given *ortho*-substituent may vary with the nature of the reaction centre, the reaction and the reaction condition, *e.g.* solvent.

The main approach to understanding the *ortho*- effect involves attempts to specify quantitatively the polar interference. Only in recent years, a more complete analysis through multiple regression on appropriate parameters become possible in some cases. Charton reviewed this field comprehensively in 1971 and analyzed 265 sets of data.

EXPERIMENTAL

All the chemicals used were of AnalaR grade. Quinolinium fluorochromate (QFC) was synthesised by the method described in literature[18]. All the *ortho*-substituted phenyl methyl sulphides were obtained by the methylation of the corresponding thiols which were obtained from the respective *ortho*-substituted anilines[19]. The purity was ascertained by the spectroscopic methods. Solvents were purified by the usual methods[20]. All the experiments were carried out under pseudo-first-order conditions by keeping the substrate always in excess. The reaction mixture was homogeneous throughout the reaction and the kinetics was followed by observing the decrease in absorption of QFC at 350 nm employing a Jasco 7200 UV-visible spectrophotometer with a variable temperature accessory. In the case of nitro compounds, the reactions were followed iodometrically. Duplicate kinetic runs showed that the rate constants obtained by the two methods agreed within ± 3%. Computations of the rate constants were made from the plot of log absorbance *vs.* time. All the rate constants are average of two or more determinations.

Stoichiometry and Product Analysis

The stoichiometric runs carried out in presence of excess of QFC at 35°C reveal that two mol of the oxidant are consumed by three mol of sulphide.

$$3R_2S + 2(C_9H_7NH)CrO_3F + H_2O \longrightarrow 3R_2SO + 2(C_9H_7NH)CrO(OH)F$$

The reaction mixture was analysed by Co-TLC. The reaction mixture was extracted with chloroform in an actual kinetic run after about 80% completion of the reaction. The solvent was removed at reduced pressure after drying over anhydrous sodium sulphate. The reaction mixture was monitored by TLC (silica gel) and developed by benzene-ethyl acetate mixture (80% benzene) along with spots of authentic samples of methyl phenyl sulphide, methyl phenyl sulphoxide and methyl phenyl sulphone. The reaction mixtures gave two spots which were made visible by exposure to iodine. They exactly corresponded to the R_f values of the authentic samples of sulphide and sulphoxide.

RESULTS AND DISCUSSION

The rate coefficients of oxidation and the activation parameters are listed in Table-1. Regression analysis has been carried out with Taft's linear free-energy, polar-energy relationship (eqn. A) and linear free-energy, steric-energy relationship (eqn. B).

$$\log k_{ortho} = \rho_0^* \sigma_0^* + h \qquad (A)$$

$$\log k_{ortho} = \delta E_s + h \qquad (B)$$

σ_0^* (polar) and E_s (steric) are the substituent constants. ρ_0^* is a reaction constant analogous to ρ and δ is a steric susceptibility constant. The results of the regression analysis in the light of the Taft's relationship are expressed by the following equations.

$$\log k_{ortho}(20°C) = -0.346\sigma_0^* - 2.500 \qquad (1)$$

$$(r = 0.805; s = 0.133; n = 5)$$

$$\log k_{ortho}(20°C) = 0.143 E_s - 2.160 \qquad (2)$$

$$(r = 0.455; s = 0.200; n = 5)$$

r = correlation coefficient

s = standard deviation

n = number of data points

TABLE-1
RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE OXIDATION OF *ORTHO*-SUBSTITUTED PHENYL METHYL SULPHIDES WITH QFC

[QFC = 2.70×10^{-4} mol dm^{-3}]; [TsOH] = 1.35×10^{-2} mol dm^{-3};
[Sulphide] = 7.95×10^{-3} mol dm^{-3}

No.	Substituent	$*k' \times 10^3$ Temp. (°C)			$\Delta H^{\#}$ kJ mol^{-1}	$-\Delta S^{\#}$ J K^{-1} mol^{-1}	$-\Delta S^{\#}$ J K^{-1} mol^{-1}	r	SD
		20	35	45					
1.	H	8.32	47.50	95.70	74.32	30.61	83.74	0.994	0.244
2.	*o*-CH_3	4.89	16.20	40.20	62.91	74.78	85.94	0.999	0.052
3.	*o*-OCH_3	2.96	13.60	26.40	65.86	68.21	86.86	0.993	0.186
4.	*o*-Br	2.19	6.94	14.60	56.15	104.31	88.28	0.999	0.032
5.	*o*-Cl	1.98	5.68	10.90	50.58	125.85	89.34	0.999	0.017
6.	*o*-NO_2	1.51	2.60	3.43	23.06	220.05	90.83	0.994	0.058

$*k' = \dfrac{k_{obs}}{[\text{sulphide}]^n}$ where n is the order wrt sulphide

The very poor correlation with equation (B) indicates that minor role of the primary steric effect or the bulk effect.

The above single parameter equation did not give satisfactory correlations. According to the modern view on the treatment of steric effect, Gallo[21] suggested that the single parameter treatment is unlikely to be of any general use. The linear free energy-polar and steric-energy relationship is in principle the most general equation since the roles of both polar and steric effects are considered.

$$\log k_{ortho} = \rho_0^* \sigma_0^* + \delta E_s + h \qquad \text{(C)}$$

$$\log k_{ortho}(20°C) = \underset{(\pm 0.043)}{-0.852\sigma_0^*} - \underset{(\pm 0.031)}{0.413E_s} - 2.313 \qquad (3)$$

$$R = 0.998;\ SE = 0.017;\ n = 5;\ CL > 99\%$$

where

R = Multiple correlation coefficient

SE = Standard error of regression

CL = F-Test confidence limit

Percentage of polar component = $P\sigma_0^* = 67.35$
Percentage of steric component = $PE_s = 33.65$

Multiple correlation using equation (C) is highly successful. The results indicate that steric contribution seems to be much less than the polar effects of the *ortho*-substituents.

To understand the composition of localized (L), delocalized (D) and steric effects (S) operating in these reactions, the rate data are analyzed with LD and LDS equations[22, 23] (D and E).

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

$$\log k_{ortho} = L\sigma_I + D\sigma_R + S\nu + h \qquad \text{(E)}$$

where σ_I, σ_R and ν are inductive, resonance and steric substituent constants respectively. In the analysis, all the four σ_R scales are employed. The values of σ_I, σ_R and ν are those compiled by Aslam et *al*[24]. The steric parameter ν is defined as

$$\nu_x = r_{Vx} - r_{VH} = r_{Vx} - 1.2 \qquad (4)$$

r_{Vx} and r_{VH} are the van der Waals' radii[25]. The steric parameter ν was chosen in preference to Taft's E_s values. Charton[25] has demonstrated a linear relationship between E_s and van der Waals' radii. The major obejctive of this investigation is to detect the presence or absence of steric effects and to determine the composition of electrical effects.

LD Equation: 100R values are *ca.* 95. The parent system does not conform well to the regressions. Correlation improves much better when the parent is excluded from the correlation analysis. h_{obsd} value at 20°C is equal to −2.200 (σ_I, σ_R^0 correlation). h value (the data point for the unsubstituted member of the set) is −2.079. The h_{obsd} values are close to h and this clearly shows that the data set belongs to case 4 of Charton's classification ($h_{obsd} = h$).

To test the significance of the three substituent constants multiple linear regression analyses were carried out with σ_I and σ_R^0, σ_I and ν and σ_R^0 and ν. The absence of excellent correlation shows that all the three substituent constants are significant.

σ_I, σ_R^0 Correlation:

$$\log k_{ortho}\,(20°C) = -0.957\sigma_I + 0.189\sigma_R^0 - 2.200 \qquad (5)$$

100R = 95.62; SE = 0.104; Ψ = 0.41; n = 6

σ_I, ν correlation (NO_2–Planar):

$$\log k_{ortho}\,(20°C) = 0.783\sigma_I - 0.124\nu - 2.207 \qquad (6)$$

100R = 95.50; SE = 0.145; Ψ = 0.175; n = 6

NO_2 (orthogonal):

$$\log k_{ortho}\,(20°C) = -0.824\sigma_I - 0.343\nu - 2.127 \qquad (7)$$

100R = 98.10; SE = 0.069; Ψ = 0.273; n = 6

σ_R^0, ν Correlation (NO_2–Planar):

$$\log k_{ortho}\,(20°) = 0.689\sigma_R^0 - 0.633\nu - 2.045 \qquad (8)$$

100R = 93.06; SE = 0.130; Ψ = 0.267; n = 6

NO_2 (orthogonal):

$$\log k_{ortho}\,(20°) = -0.289\sigma_R^0 - 0.841\nu - 2.216 \qquad (9)$$

100R = 65.65; SE = 0.269; Ψ = 1.066; n = 6

LDS Equation: LDS equation gives a very successful correlation. This is justified by high values of F, 100R, minimum SE and Ψ values in the Exner's scale. Exner's Ψ is a measure of goodness of fit, and in the Exner scale the fit is poor but under admissible limit[26]. The negative regression coefficient for the steric term corresponds to the reaction being subject to steric retardation by the *ortho*-substituent. Significance of correlation is tested by means of F test. Meaningful correlation (> 90% Cl) indicates that the set may belong to case 1, case 3 or case 4 of Charton's classification. Confidence level of t-test of S is <90% and this rules out case 1. The h_{obsd} values are very close to the h value. The respective h_{obsd} and h values are –2.098 and –2.079 (σ_I, σ_R^0 correlation). The data set belongs to case 4 of Charton's classification.

$$\text{The values of } P_L \left[P_L = \frac{100\,|L|}{|L| + |D| + |S|} \right],$$

per cent localized contribution to the overall effects, are useful in describing the composition of the electrical effect. The advantage of P_L is that its value is within the range 0–100. P_D is the per cent composition of the declocalized effect.

$$P_D = \frac{100\,|D|}{|L| + |D| + |S|}$$

A better description of the composition of steric effect is given by 'per cent steric factor', P_S, where

$$P_S = \frac{100\,|S|}{|L| + |D| + |S|}$$

σ_I, σ_R^0, ν correlation; NO_2-orthogonal at 35°C:

$P_L = 49.75$

$P_D = 19.85$ F-test: > 90% CL

$P_S = 30.40$

σ_I, σ_R^0, ν correlation; NO_2-Planar at 35°C

$P_L = 36.50$

$P_D = 24.31$ F-test: > 95% CL

$P_S = 39.19$

Although electrical effects are predominant, small but significant steric effects are observed in the reaction.

The linear relation between $\Delta H^{\#}$ and $\Delta S^{\#}$ (Fig. 1) ($r = 0.998$; $s = 1.040$) suggests the operation of a similar mechanism in all the *ortho*-substituted sulphides studied. Excellent correlation with Exner plot (plot of $\log k_{(T_2)}$ *vs.* $\log k_{(T_1)}$) (Fig. 2) ($r = 0.990$; $s = 0.076$) confirms the above view.

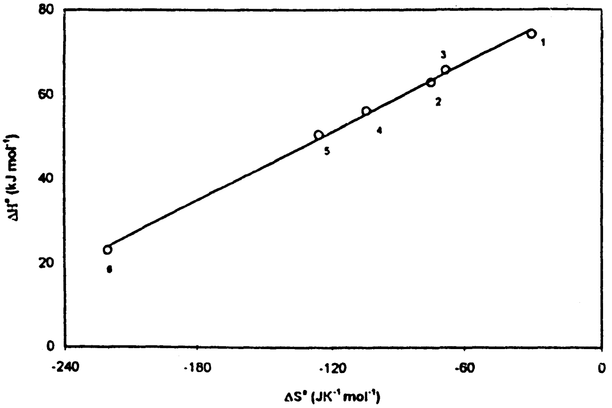

Fig 1 Isokinetic plot (Numbered as in Table 1)

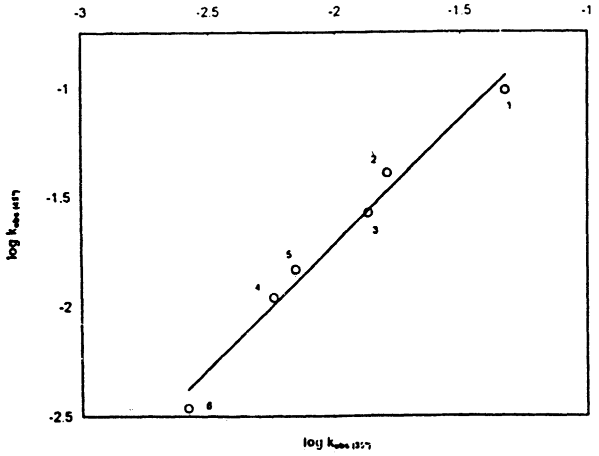

Fig. 2. The Exner plot (Numbered as in Table 1)

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