

Kinetics and correlation analysis of reactivity in the oxidation of organic sulfides by butyltriphenylphosphonium dichromate

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Abstract. The oxidation of a number of monosubstituted aryl methyl, alkyl phenyl, dialkyl, and diphenyl sulfides by butyltriphenylphosphonium dichromate (BTPPD), to the corresponding sulfoxides, is first order with respect to BTPPD and is second order with respect to sulfide. The reaction is catalysed by hydrogen ions and the dependence is of second order. The oxidation of *meta*- and *para*-substituted aryl methyl sulfides correlated best in terms of Hammett equation, the reactions exhibited negative polar reaction constant. The *ortho*-substituted compounds correlated best in terms of Charton's triparametric equation with negative polar constant and a small degree of steric hindrance. The oxidation of alkyl phenyl sulfides exhibited a good correlation in terms of Pavelich–Taft equation confirming that the electron-donating power of the alkyl group increases the rate, however, the reactivity is not markedly controlled by the bulkiness of the alkyl group. The rates of oxidation of sulfides were determined in nineteen organic solvents. An analysis of the solvent effect by multi-parametric equations indicated the relatively greater importance of the cation-solvating power of the solvents. A mechanism involving a single-step electrophilic oxygen transfer from BTPPD to the sulfide leading to polar transition state has been proposed.

Keywords. Kinetics; mechanism; sulfides; oxidation; correlation analysis; Cr(VI) complex.

1. Introduction

Selective oxidation of organic compounds under non-aqueous conditions is an important transformation in synthetic organic chemistry. For this, a number of different chromium (VI) derivatives have been reported.^{1,2} Butyltriphenylphosphonium dichromate (BTPPD), a Cr(VI) derivative, reported to be a mild and selective oxidant.³ It oxidizes amines to azo-compounds, thiols to disulphides and regenerates carbonyl compounds from their oximes. We have been interested in the kinetics and mechanism of the oxidation by BTPPD and a few reports have emanated from our laboratory.^{4–7} There seems to be no report on the mechanistic aspects of the oxidation of organic sulfides by BTPPD. In this paper, we report the kinetics of the oxidation of 34 organic sulfides by BTPPD in dimethyl sulfoxide (DMSO) as the solvent, with emphasis on structure-reactivity correlation. The mechanistic aspects are discussed.

2. Experimental

2.1 Materials

The preparation, purification and specification of the sulfides have been described before.⁸ BTPPD was prepared by the reported method³ and its purity was checked by an iodometric method. The solvents were purified by the reported methods.⁹ (Amongst the solvents, CS₂ is a flammable liquid and is toxic). Toluene *p*-sulphonic acid (TsOH) was used as a source of hydrogen ions.

2.2 Product analysis

Methyl phenyl sulfide (0.01 mol) and BTPPD (0.01 mol) were dissolved in DMSO (50 ml) and the mixture was allowed to stand for approximately 20 h in the presence of 1.0 mol dm⁻³ TsOH. Most of the solvent was removed under reduced pressure. The residue was diluted with water and extracted with chloroform (3 × 50 ml). The chloroform layer was dried over anhydrous MgSO₄, the solvent was re-

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moved by evaporation and the residue was analysed by IR and ^1H NMR spectroscopy. The spectra were identical with those of MeSOPh. Peaks characteristic of MeSPh and MeSO_2Ph could not be detected. Similar experiments were performed with other aryl methyl sulfides also. In all cases, the products were the corresponding sulfoxide only.

2.3 Stoichiometry

To determine the stoichiometry, BTPPD (0.006 mol) and different sulfides (0.001 mol) were made up to 100 ml in DMSO in the presence of 1.0 mol dm^{-3} TsOH, in different experiments. The reaction was allowed to stand for 12 h to ensure the completion of the reaction. The residual BTPPD was determined spectrophotometrically. Several determinations with different concentrations of BTPPD and sulfide showed that the reaction exhibited 1:3 stoichiometry i.e. one mole of BTPPD was consumed with three moles of sulfide.

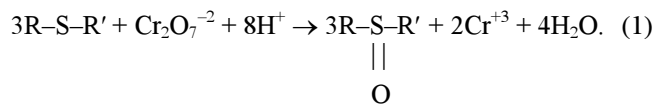
2.4 Kinetic measurements

Pseudo-first order conditions were attained by keeping a large excess ($\times 10$ or greater) of the sulfides over the oxidant. The reactions were carried out at constant temperature ($\pm 0.1 \text{ K}$). Lower than the ambient temperature was obtained with the refrigerated bath circulator. The solvent was DMSO, unless stated otherwise. The reactions were followed by monitoring the decrease in the concentration of BTPPD at 364 nm for up to 80% of the reaction. The pseudo-first order rate constant, k_{obs} , was evaluated from the linear ($r^2 > 0.995$) plots of $\log [\text{BTPPD}]$ versus time. Duplicate kinetic runs showed that the rate constants were reproducible to within $\pm 3\%$. The specific rate constant, k , was evaluated from the relation: $k = k_{\text{obs}}/[\text{sulfide}]^2 [\text{H}^+]^2$. In correlation analyses, we have used coefficient of determination (C^2 or c^2), standard deviation (sd) and Exner's parameter,¹⁰ ψ , as the measures of the goodness of fit.

3. Results

Rates and other experimental data were obtained for all the sulfides. Since the results are similar, only representative data are reproduced here.

Oxidation of organic sulfides by BTPPD resulted in the formation of the corresponding sulfides. The product analysis and the stoichiometry determination suggested the following overall reaction.



3.1 Rate laws

The reactions were found to be of first order with respect to BTPPD. In individual kinetic runs, plots of $\log [\text{BTPPD}]$ versus time were linear ($c^2 > 0.995$). Further, the pseudo-first order rate constants do not depend on the initial concentration of BTPPD (table 1). The reactions showed a second order dependence on the concentration of sulfide, as observed by the nearly constant values of $k_{\text{obs}}/[\text{sulfide}]^2$ (table 1).

3.2 Test for free radicals

Oxidation of sulfides by BTPPD, in an atmosphere of nitrogen, failed to induce polymerization of acrylonitrile. In blank experiments, with the substrate absent, no noticeable consumption of BTPPD was observed. The addition of acrylonitrile had no effect on the rate of oxidation (table 1). To further confirm the absence of free radicals in the reaction pathway, the reaction was carried out in the presence of 0.05 mol dm^{-3} of 2,6-di-*t*-butyl-4-methylphenol (butylated hydroxytoluene or BHT). It was observed that BHT was recovered unchanged, almost quantitatively.

3.3 Effect of acidity

Rates of oxidation of sulfides increase with an increase in acidity. The dependence on hydrogen ion concentration is of the form $\text{rate} = k[\text{H}^+]^2$, as observed by the nearly constant values of $k_{\text{obs}}/[\text{H}^+]^2$ (table 2).

3.4 Effect of temperature

The rates of oxidation of 34 organic sulfides were determined at different temperatures and the activation parameters were calculated (table 3).

3.5 Effect of solvent

The oxidation of methyl phenyl sulfide by BTPPD was studied in nineteen organic solvents. The solubility of the reactants and the reaction of BTPPD with primary and secondary alcohols limited the choice of solvents. There was no reaction with the chosen

Table 1. Rate constants for the oxidation of methyl phenyl sulfide by BTTPPD at 288 K.

[MeSPh] (mol dm ⁻³)	10 ³ [BTTPPD] (mol dm ⁻³)	[H ⁺] (mol dm ⁻³)	10 ⁴ <i>k</i> _{obs} (s ⁻¹)	10 ² <i>k</i> _{obs} /[sulfide] ²
0.01	1.0	1.0	0.70	70.0
0.02	1.0	1.0	2.74	68.5
0.03	1.0	1.0	6.48	72.0
0.05	1.0	1.0	18.8	75.2
0.10	1.0	1.0	71.3	71.3
0.15	1.0	1.0	158	70.2
0.20	1.0	1.0	280	70.0
0.10	0.8	1.0	72.4	
0.10	1.5	1.0	71.0	
0.10	2.0	1.0	71.6	
0.10	3.0	1.0	71.5	
0.10	5.0	1.0	72.0	
0.05	1.0	1.0	19.0*	
0.05	1.0	1.0	18.7**	

*Contains 0.005 mol dm⁻³ acrylonitrile. **Contains 0.01 mol dm⁻³ acrylonitrile

Table 2. Effect of acidity on the oxidation of phenyl methyl sulfide by BTTPPD^a.

[H ⁺]/mol dm ⁻³	0.1	0.2	0.4	0.8	1.0	2.0
10 ⁴ <i>k</i> _{obs} /s ⁻¹	0.19	0.72	3.19	11.9	18.8	71.7
10 ⁴ <i>k</i> _{obs} /[H ⁺] ²	19.0	18.0	19.9	18.6	18.8	17.9

^a[MeSPh] = 0.05 mol dm⁻³, [BTTPPD] = 0.001 mol dm⁻³, and temperature = 288 K

solvents. The kinetics were similar in all the solvents. The values of the rate constant, *k*, are recorded in table 4.

4. Discussion

The entropies and enthalpies of the activation of the oxidation of thirty-four organic sulfides were not satisfactorily correlated ($c^2 = 0.9102$). According to Exner,¹¹ an isokinetic relationship between the calculated values of the activation entropies and enthalpies is often vitiated by random experimental errors. Exner suggested an alternative method for establishing the isokinetic relationship. The correlation was tested and found genuine by applying Exner's criterion.¹¹ The Exner's plot between the values of $\log k$ at 278 K and at 308 K, for the thirty-four sulfides, is linear (slope = 0.8068 ± 0.0204 ; $c^2 = 0.9832$). The value of isokinetic temperature, determined by Exner's method, is 567 ± 57 K. A linear isokinetic relationship is, however, a necessary condition for the validity of linear free energy relationships.¹² It also implies that all the reactions, so correlated, follow a similar mechanism.

4.1 Solvent effect

The values of the rate constant, *k*, in eighteen solvents (CS₂ was not considered as the complete range of the solvent parameters are not available), was correlated in terms of linear solvation energy relationship (LSER) of Kamlet *et al.*¹²

$$\log k = A + p\pi^* + a\alpha + b\beta. \quad (2)$$

Here, π^* represents the solvent polarity for solvent-solute interaction of non-specific type, β is a scale of solvent hydrogen-bond acceptor basicity, while α represents the solvent hydrogen-bond donor acidity; A is the intercept term. It may be mentioned here that out of the 18 solvents, for 13 solvents α has a value of zero. The analyses in terms of (2), a two-parameter equation involving π^* and β , and separately with π^* and β gave the following results. Here *n* is the number of data points.

$$\log k = -2.06 + 1.57 \pm 0.20\pi^* - 0.17 \pm 0.15\alpha + 0.18 \pm 0.16\beta, \quad (3)$$

$$c^2 = 0.8572, \text{ sd} = 0.18, n = 18, \psi = 0.41$$

Table 3. Rate constants and activation parameters for the oxidation of sulfides by BTPPD.

Subst.	$10^2 k$ (mol ⁻⁴ dm ¹² s ⁻¹) at temp. (K)				ΔH^* (kJ mol ⁻¹)	ΔS^* (J mol ⁻¹ K ⁻¹)	ΔG^* (kJ mol ⁻¹)
	278 K	288 K	298 K	308 K			
(i) Aryl methyl sulfides							
H	36.0	71.3	139	267	45.0 ± 0.5	-92 ± 2	72.2 ± 0.4
p-Me	82.2	153	276	515	40.8 ± 0.7	-100 ± 2	70.4 ± 0.5
p-OMe	140	225	396	718	36.3 ± 1.5	-112 ± 5	69.5 ± 1.2
p-F	26.3	56.0	111	220	47.7 ± 0.3	-84 ± 1	72.7 ± 0.2
p-Cl	12.0	25.4	54.1	113	50.7 ± 0.7	-80 ± 2	74.5 ± 0.5
p-Br	12.1	25.2	54.2	111	50.2 ± 0.7	-82 ± 2	74.5 ± 0.6
p-NO ₂	0.78	2.37	6.23	15.2	67.8 ± 0.7	-41 ± 2	79.9 ± 0.5
p-COMe	2.79	6.98	17.0	38.4	59.8 ± 0.2	-60 ± 1	77.4 ± 0.1
p-CO ₂ Me	7.92	18.6	41.2	86.2	54.1 ± 0.3	-71 ± 1	75.2 ± 0.1
p-NHAc	38.0	73.0	141	279	44.7 ± 0.9	-92 ± 3	72.1 ± 0.7
p-NH ₂	958	1295	1930	3138	25.6 ± 1.8	-135 ± 6	65.6 ± 1.4
m-Me	49.9	93.4	178	341	43.1 ± 0.8	-96 ± 3	71.5 ± 0.7
m-OMe	21.6	44.5	91.3	182	48.1 ± 0.5	-85 ± 2	73.2 ± 0.4
m-Cl	5.71	13.6	30.9	66.7	55.8 ± 0.1	-68 ± 1	75.9 ± 0.1
m-Br	5.42	13.1	29.7	64.8	56.3 ± 0.1	-67 ± 1	76.0 ± 0.1
m-I	8.95	20.4	44.1	97.5	53.9 ± 0.6	-71 ± 2	75.0 ± 0.5
m-NO ₂	1.10	3.20	8.32	19.0	65.2 ± 0.8	-48 ± 3	79.3 ± 0.7
m-CO ₂ Me	6.38	14.9	35.0	75.0	56.2 ± 0.4	-66 ± 1	75.6 ± 0.3
o-Me	20.6	43.0	88.3	180	48.9 ± 0.6	-82 ± 2	73.3 ± 0.5
o-OMe	13.6	27.1	53.1	105	45.9 ± 0.6	-97 ± 2	74.5 ± 0.5
o-NO ₂	1.30	3.31	7.69	16.8	58.2 ± 0.3	-72 ± 1	79.4 ± 0.2
o-CO ₂ Me	138	333	735	1565	55.0 ± 0.2	-44 ± 1	68.1 ± 0.1
o-NH ₂	31.7	60.1	110	213	42.4 ± 0.9	-102 ± 3	72.7 ± 0.7
o-Cl	3.25	7.47	16.2	35.1	53.8 ± 0.4	-80 ± 1	77.5 ± 0.3
o-Br	2.85	6.81	15.3	32.5	56.8 ± 0.6	-70 ± 2	77.6 ± 0.5
o-I	2.62	6.21	14.2	32.1	57.1 ± 0.6	-70 ± 2	77.8 ± 0.5
o-CN	1.82	4.61	10.6	21.9	56.6 ± 0.7	-75 ± 2	78.6 ± 0.6
(ii) Alkyl phenyl sulfides							
Et	52.4	102	195	373	44.0 ± 0.5	-92 ± 2	71.3 ± 0.4
Pr	39.2	78.9	156	304	46.1 ± 0.4	-87 ± 2	71.9 ± 0.4
i-Pr	48.6	97.3	194	375	46.0 ± 0.4	-86 ± 1	71.4 ± 0.3
t-Bu	21.3	49.9	108	226	53.4 ± 0.1	-66 ± 1	72.8 ± 0.1
(iii) other sulfides							
Me ₂ S	74.3	145	288	550	45.1 ± 0.6	-85 ± 2	70.4 ± 0.5
Pr ₂ S	140	295	530	851	40.3 ± 1.4	-97 ± 5	69.0 ± 1.2
Ph ₂ S	5.05	9.75	22.8	42.1	48.8 ± 1.5	-95 ± 5	76.8 ± 1.2

$$\log k = -2.00 + 1.63 \pm 0.19\pi^* + 0.12 \pm 0.16\beta \quad (4)$$

$$c^2 = 0.8441, \text{sd} = 0.18, n = 18, \psi = 0.42$$

$$\log k = -2.03 + 1.66 \pm 0.18\pi^* \quad (5)$$

$$c^2 = 0.8285, \text{sd} = 0.19, n = 18, \psi = 0.41$$

$$\log k = -2.96 + 0.41 \pm 0.36\beta \quad (6)$$

$$c^2 = 0.0776, \text{sd} = 0.43, n = 18, \psi = 0.99$$

The results show that *ca.* 86% of the data on the solvent effect is explained by (2). According to Exner's

criterion,¹⁰ however, the correlation is poor. The major contribution is from the solvent polarity term, π^* . Both α and β play relatively insignificant roles. There is no significant collinearity between π^* and β for the eighteen solvents ($c^2 = 0.0477$, $\text{sd} = 0.24$).

The data on solvent effect were analysed in terms of Swain's equation¹³ also, where A represents the anion-solvating power of the solvent and B the cation-solvating power; C is the intercept term, and (A + B) is postulated to represent the solvent polarity.

$$\log k = aA + bB + C. \quad (7)$$

Table 4. Rate constants for the oxidation of methyl phenyl sulfide by BTPPD in different solvents at 288 K.

Solvent	$10^2 k$ (mol ⁻⁴ dm ¹² s ⁻¹)	Solvent	$10^2 k$ (mol ⁻⁴ dm ¹² s ⁻¹)
Chloroform	20.2	Tetrahydrofuran	11.6
1,2-Dichloroethane	25.0	<i>tert</i> -butylalcohol	8.35
Dichloromethane	22.7	Dioxane	11.9
DMSO	71.3	1,2-Dimethoxyethane	6.15
Acetone	22.2	Acetic acid	3.68
DMF	36.8	Ethyl acetate	8.72
Butanone	16.5	Carbon disulfide	3.35
Nitrobenzene	27.6		
Benzene	8.22		
Cyclohexane	0.87		
Toluene	6.65		
Acetophenone	29.9		

The results of the correlation analyses in terms of (7), individually with A and B, and with (A + B) are given below.

$$\log k = 0.55 \pm 0.01A + 1.70 \pm 0.01B - 2.17 \quad (8)$$

$$c^2 = 0.9998, \text{ sd} = 0.01, n = 19, \psi = 0.02$$

$$\log k = 0.31 \pm 0.56A - 2.99 \quad (9)$$

$$c^2 = 0.0181, \text{ sd} = 0.45, n = 19, \psi = 1.0$$

$$\log k = 1.65 \pm 0.10B - 2.01 \quad (10)$$

$$c^2 = 0.9436, \text{ sd} = 0.11, n = 19, \psi = 0.24$$

$$\log k = 1.32 \pm 0.15(A + B) - 2.14 \quad (11)$$

$$c^2 = 0.8273, \text{ sd} = 0.19, n = 19, \psi = 0.43.$$

The data on solvent effect showed an excellent correlation in terms of Swain's equation¹³ with both anion- and cation-solvating powers contributing to the observed solvent effect. However, the role of cation-solvation is major, it alone accounts for *ca.* 94% of the data. There is no significant collinearity between A and B for the nineteen solvents ($c^2 = 0.0108$; $\text{sd} = 0.27$). The solvent polarity, represented by (A + B) accounted for *ca.* 83% of the data. In view of the fact that *ca.* 83% of the data is accounted for by (A + B), an attempt was made to correlate the data with the relative permittivity of the solvents. A plot of $\log k$ against the inverse of the relative permittivity, however, is not linear ($c^2 = 0.5078$).

The solvent polarity term of Kamlet's equation¹² explained *ca.* 83% of the data. Thus it seems that the solvent polarity terms of the two equations represent nearly the same solvent property. This is borne out by the fact that there is a significant collinearity between π^* and (A + B) for the eighteen solvents ($c^2 = 0.7811$).

Table 5. Correlation of the rates of the oxidation of *meta*- and *para*-substituted aryl methyl sulfides in Hammett equation^a.

Temp./K	ρ	R^2	sd	Ψ
278	-2.12 ± 0.03	0.9975	0.039	0.051
288	-1.89 ± 0.02	0.9974	0.035	0.052
298	-1.71 ± 0.02	0.9972	0.033	0.054
308	-1.59 ± 0.02	0.9964	0.035	0.062

^aNo. of data points = 18

The solvent effect suggests that the transition state is more polar than the reactants. This indicates an attack of electrophilic BTPPD-oxygen on electron-rich sulfur resulting in the formation of positive polarisation of sulfur atom and negative polarisation of oxygen atom. The increased polarity of the transition state implies the increase in rate with an increase in the polarity of the solvent. This is justified by observed rate data.

4.2 Correlation analysis of reactivity

The rates of oxidation of *meta*- and *para*-substituted aryl methyl sulfides correlate well with Hammett¹⁴ substituent constant yielding negative reaction constant (table 5). The negative reaction constant points to a generation of electron-deficient centre in the transition state indicating an electrophilic attack of BTPPD on sulfur atom. The magnitude of reaction constant is smaller than those observed in the oxidation reactions proceeding via the formation of halogenosulfonium cation in the rate-determining step. The values of ρ for the formation of RArSCI^+ and RArSBr^+ were -4.25 and -3.20 respectively.^{15,16} This indicates that in the transition state of the present

Table 6. Correlation of rate of oxidation of alkyl phenyl sulfides by BTPPD in terms of Pavelich–Taft equation^a.

Temp./K	ρ^*	δ	R^2	sd	Ψ
278	-2.02 ± 0.01	-0.54 ± 0.01	0.9999	0.001	0.013
288	-1.86 ± 0.03	-0.46 ± 0.01	0.9998	0.003	0.018
298	-1.78 ± 0.04	-0.42 ± 0.01	0.9995	0.005	0.029
308	-1.72 ± 0.03	-0.38 ± 0.01	0.9996	0.002	0.026

^aNo. of data points = 5

reaction, the electron-deficiency on the sulfur atom is not very high, but similar to that observed in the oxidation of sulfides by periodate ion¹⁷ ($\rho = 1.40$), permanganate¹⁸ (-1.52) and pyridinium fluorochromate¹⁹ (-1.65), where the oxidation of sulfides is involving a direct oxygen transfer via an electrophilic attack on the sulfide–sulfur.

The rates of oxidation of alkyl phenyl sulfides did not yield any significant correlation separately with Taft's σ^* or E_s values.¹⁴ The rates were, therefore, analysed in terms of Pavelich–Taft's²⁰ dual-substituent parameter (DSP) (12).

$$\log k = \rho^* \sigma^* + \delta E_s + \log k_0 \quad (12)$$

The correlations are excellent (table 6). Though the number of compounds is small (five) for an analysis by a DSP equation, the results can be used qualitatively. The negative polar reaction constant confirms the generation of electron-deficient centre in the rate-determining step, resulting in an enhancement of the reaction rate with an increase in the electron-donating power of the alkyl group. The steric effect plays a minor inhibitory role.

The rates of oxidation of ortho-substituted aryl methyl sulfides did not yield a significant correlation with either Taft's polar or steric substituent constants.²¹ The rates were, therefore, analysed in terms of Charton's (13) and (14).²² Here, σ_1 , σ_R and V represents field, resonance and steric substituent constants, respectively. The values used were those compiled by Aslem *et al.*²³

$$\log k = \alpha \sigma_1 + \beta \sigma_R + h, \quad (13)$$

$$\log k = \alpha \sigma_1 + \beta \sigma_R + \phi V + h. \quad (14)$$

In multiple linear regression, using (13), the coefficient of multiple correlation is poor and the sd is high (15). The coefficient of correlation is also poor in terms of (14), if all the ortho compounds are included (16). However, the correlation improves substantially if the rate data of o-COOMe is not included (17).

$$\log k = -1.98 \pm 0.77 \sigma_1 + 0.28 \pm 0.59 \sigma_R + 0.66 \quad (15)$$

$$c^2 = 0.4916, \text{sd} = 0.50, n = 10, \psi = 0.79, T = 308 \text{ K}$$

$$\log k = -1.96 \pm 0.91 \sigma_1 + 0.27 \pm 0.64 \sigma_R - 0.06 \pm 0.94V + 0.67 \quad (16)$$

$$c^2 = 0.4920, \text{sd} = 0.54, n = 10, \psi = 0.85, T = 308 \text{ K}$$

$$\log k = -1.50 \pm 0.02 \sigma_1 - 0.39 \pm 0.01 \sigma_R - 0.49 \pm 0.02V - 0.43 \quad (17)$$

$$c^2 = 0.9996, \text{sd} = 0.01, n = 9, \psi = 0.03$$

The behaviour of o-NO₂ is consistent with the planar confirmation.

The deviations noted in the case of o-COOMe substituted compound can be attributed to the moderate anchimeric assistance provided by this group to the reaction by stabilising the positively polarised sulfur in the transition state. The values of k for the oxidation of o-COOMe substituted sulfides, calculated by (14), is $44.4 \times 10^{-2} \text{ mol}^{-4} \text{ dm}^{12} \text{ s}^{-1}$, whereas the observed value is $1565 \times 10^{-2} \text{ mol}^{-4} \text{ dm}^{12} \text{ s}^{-1}$. The rate-enhancement observed may be caused due to neighbouring group participation.

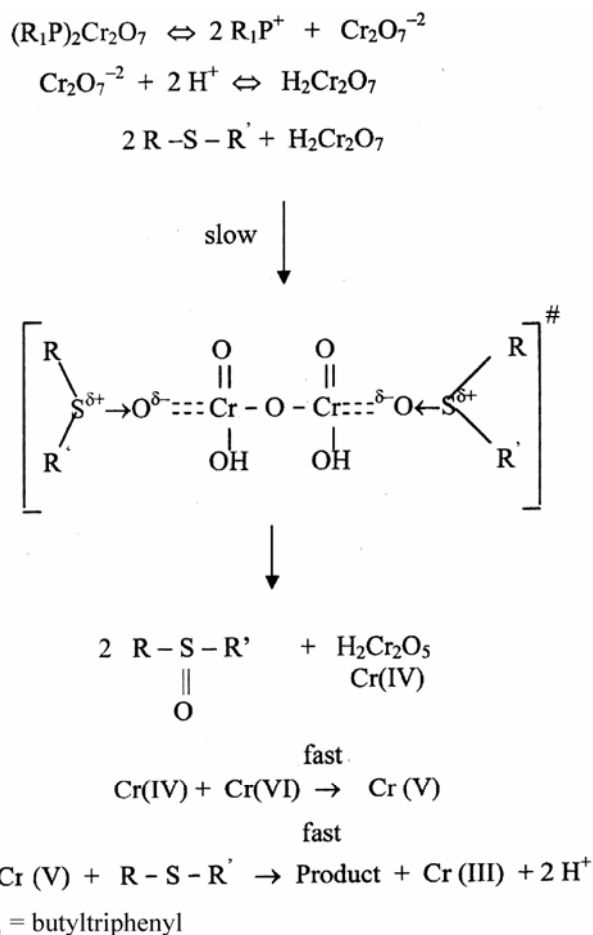
The reaction constants and other statistical data for the ortho-substituted aryl methyl sulfides are reported in table 7. The contribution of the resonance effect to the polar effects, P_R , and that of steric effect to the total effect of the ortho group, P_S , were calculated by Charton's method.²² The results showed that, in the oxidation of ortho-compounds also the field effect is predominating as in the case of meta- and para-substituted aryl methyl sulfides. The resonance and steric effects play relatively a minor role.

4.3 Mechanism

A one-electron oxidation, giving rise to free radicals, is unlikely in view of the failure to induce polymerisation of acrylonitrile. BHT is an excellent trap for free radicals.²⁴ The fact that BHT was

Table 7. Correlation of the rates of the oxidation of *ortho*-substituted aryl methyl sulfides by Charton's method.

T/K	α	β	ϕ	R^2	sd	P_s	P_R	Ψ
278	-1.71 ± 0.01	-0.59 ± 0.01	-0.70 ± 0.01	0.9998	0.008	23.3	25.7	0.012
288	-1.60 ± 0.02	-0.50 ± 0.02	-0.64 ± 0.02	0.9995	0.014	23.4	24.3	0.027
298	-1.53 ± 0.02	-0.42 ± 0.02	-0.56 ± 0.02	0.9994	0.015	22.5	21.9	0.030
308	-1.50 ± 0.02	-0.39 ± 0.01	-0.49 ± 0.02	0.9996	0.012	20.9	21.2	0.027

**Scheme 1.**

recovered unchanged also goes against the occurrence of a one-electron oxidation.

The analysis of the solvent effect indicated the importance of the cation-solvating power of the solvent. The observed results can be explained on the basis of two alternative mechanisms. BTPPD may be ionised in DMSO to butyltriphenylphosphonium and dichromate ions. The formation of a cation is supported by the major role of the cation-solvating power of the solvent. The dichromate ion undergoes diprotonation followed by a rate-determining electrophilic attack of BTPPD-oxygen to electron-rich sulfur to produce the corresponding sulfoxide via an S_N2 type transition state (scheme 1). A low magni-

tude of polar reaction constant and the moderate degree of anchimeric assistance by the neighbouring groups also support a transition state depicted in the scheme 1, rather than the formation of sulphonium ion. The S_N2 type transition state is also supported by the solvent effect. Alternatively, BTPPD may get diprotonated first which then undergoes a rate-determining nucleophilic attack of a electron-rich sulfur atom on BTPPD oxygen atom resulting in a oxygen atom transfer to sulfide molecule to give the corresponding sulfoxide (scheme 2). The similar type of mechanism involving oxygen atom transfer in the rate-determining step is also suggested in the oxidation of sulfides by pyridinium fluorochromate (PFC)¹⁹ and hydrogen peroxide.²⁵ The rate-determining step may be viewed as an S_N2 process. The solvent effect supports the protonation step as well as a S_N2 like transition state. The value of entropy of activation in this reaction is close to the values observed in the reactions involving oxygen atom transfer.^{19,25} This supports the proposed mechanism. It may be mentioned here that though the step of the diprotonation is shown as a single-step, it must be taking place in two steps.

Initially Cr(VI) is reduced to Cr(IV). It is likely to react with another Cr(VI) to generate Cr(V) which is then reduced in a fast step to the ultimate product Cr(III). Such a sequence of reactions in Cr(VI) oxidations is well known.²⁶

The oxidation of sulfides by BTPPD may involve a cyclic intermediate as well, as has been suggested in many reactions of Cr(VI).²⁷ However, a cyclic intermediate may also exhibit a sulfurane structure. The cyclic intermediate would be highly strained in view of the apical position of a lone pair of electrons or an alkyl group. The steric requirements of the reaction, involving a cyclic intermediate, would be higher as compared to those of reactions involving S_N2 type intermediate and the observed small values of steric reaction constant are thus consistent with the proposed acyclic sulfurane mechanism. The formation of cyclic sulfurane intermediate also entails a more exacting specificity orientation and should result in a much larger entropy of activation than

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