

Oxidation of some Organic Sulfides by Pyridinium Dichromate: A Kinetic & Mechanistic Approach

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ABSTRACT: The oxidation of organic sulfides by pyridinium dichromate (PDC) resulted in the formation of the corresponding sulfoxides. The reaction is first order with respect to PDC. A Michaelis-Menten type kinetics was observed with respect to the reactants. The reaction is catalysed by toluene-p-sulfonic acid (TsOH). The oxidation was studied in nineteen different organic solvents. An analysis of the solvent effect by Swain's equation showed that the both cation- and anion-solvating powers of the solvents play important roles. The correlation analyses of the rate of oxidation of thirty four sulfides were performed in terms of various single and multiparametric equations. For the aryl methyl sulfides, the best correlation is obtained with Charton's LDR and LDRS equations. The oxidation of alkyl phenyl sulfides exhibited a very good correlation in terms of Pavelich-Taft equation. The polar reaction constants are negative indicating an electron-deficient sulfur centre in the rate-determining step. A mechanism involving formation of a sulphenium cation intermediate in the slow step has been proposed.

Key words: Correlation analysis, dichromate, kinetics, mechanism, oxidation

1. INTRODUCTION:

In synthetic organic chemistry Chromium salts have long been used as an oxidants for organic compounds. Most of the chromium salts are non-selective and drastic in nature. Further, they are insoluble in most organic solvents. Thus miscibility is a problem. To overcome these limitations, a large number of organic derivatives of Cr(VI) have been prepared and used in organic synthesis as mild and selective oxidants in non-aqueous solvents[1], one of such compounds is pyridinium dichromate (PDC)[2]. We have been interested in the kinetic and mechanistic aspects of the oxidation by complex salts of Cr(VI) and several reports on halochromates have already emanated from our laboratory[3-6]. It is, known that mode of oxidation depends upon the nature of counter-ion attached to the chromium anion. Karunakaran et. al.[7] have reported a common mechanism for the oxidation of diphenyl sulfide by various Cr(VI) reagents in acetic acid. In the present article, we report the kinetics of oxidation of thirty-four organic sulfides by PDC in dimethylformamide (DMF) as solvent. Attempts have been made to correlate rate and structure in this reaction. A probable mechanism has been proposed.

2. MATERIALS AND METHODS:

2.1 Materials:

The sulfides were either commercial products or prepared by known methods[8] and were purified by distillation under reduced pressure or crystallisation. Their purity was checked by comparing their boiling or melting points with the literature values. PDC was prepared by the reported method[2]. Toluene-p-sulfonic acid (TsOH) was used as a source of hydrogen ions.

2.2 Product Analysis:

MeSPh or Me₂S (0.1 mol) and PDC (0.01 mol) was dissolved in DMF (50 ml) and the mixture was allowed to stand for *ca.* 20 h. 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 magnesium sulfate, the solvent was removed by evaporation and the residue was analysed by IR and ¹H NMR spectroscopy. The spectra were identical with those of the corresponding sulfoxides. Peaks characteristic of the sulfide and sulfone could not be detected. In IR spectra, the product showed a strong and broad absorption at 1050 cm⁻¹. No band either at 1330 or 1135 cm⁻¹, characteristic of sulfones[9] was seen. In NMR spectroscopy, studied in the case of Me₂S, the peak due to methyl protons shifted from 2.1 ppm, in the sulfide, to 2.6 ppm in the product. In the corresponding sulfone, the peak should have appeared at 3.0 ppm[10]. Similar experiments were performed with the other sulfides also. In all cases, the products were the corresponding sulfoxides.

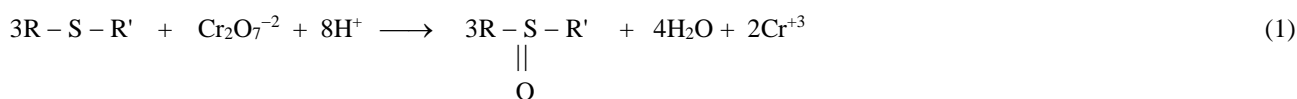
2.3 Kinetic Measurements:

The reactions were studied under pseudo-first-order conditions by keeping an excess (× 15 or greater) of the sulfide over PDC. The solvent was DMF, unless mentioned otherwise. The reactions were studied at constant temperature (±0.1 K) and were followed by monitoring the decrease in the concentration of PDC at 352 nm for up to 80% reaction extent. Pseudo-first-order rate constants, *k*_{obs},

were evaluated from linear plots ($r^2 > 0.995$) of $\log [\text{PDC}]$ against time. Duplicate kinetic runs showed that the rate constants are reproducible to within $\pm 3\%$. All kinetic runs, except those for studying the effect of acidity, were studied in the absence of TsOH. The values of the second order rate constants were computed from the relation $k_2 = k_{\text{obs}}/[\text{sulfide}]$. Simple and multivariate regression analyses were carried out by the least-squares method.

3. RESULTS AND DISCUSSION:

The oxidation of organic sulfides by PDC resulted in the formation of the corresponding sulfoxides. The overall reaction may be represented as equation (1).



3.1 Rate Laws:

The reactions were found to be first order with respect to PDC. Figure 1 depicts a typical kinetic run. The individual kinetic runs were strictly first order to PDC. Further, the first-order rate coefficients did not vary with the initial concentration of PDC. The order with respect to sulfide also was found to be one (Table 1).

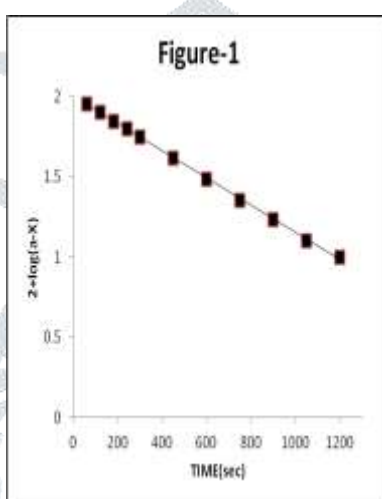


Figure 1. – Oxidation of Methyl phenyl sulfide by PDC: A typical Kinetic Run

3.2 Test for free radicals:

The oxidation of methyl phenyl sulfide, in an atmosphere of nitrogen, failed to induce the polymerization of acrylonitrile. Further, 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.

Table 1. Rate constants for the oxidation of methyl phenyl sulfide by PDC at 298 K

$10^3 [\text{PDC}]$ ----- (mol dm^{-3})	[Sulfide] ----- (mol dm^{-3})	[TsOH] ----- (mol dm^{-3})	$10^4 k_{\text{obs}}$ ----- (S^{-1})
1.0	0.10	0.0	2.07
1.0	0.20	0.0	4.16
1.0	0.40	0.0	8.31
1.0	0.60	0.0	12.6
1.0	0.80	0.0	16.2
1.0	1.00	0.0	19.8
2.0	0.40	0.0	8.55
4.0	0.40	0.0	8.19

6.0	0.40	0.0	8.64
8.0	0.40	0.0	8.28
1.0	0.20	0.0	4.41*
a contained 0.001 M acrylonitrile			

3.3 Effect of acidity:

The reaction is catalysed by TsOH (Table 2). The TsOH-dependence has the form $k_{\text{obs}} = a + b [\text{TsOH}]$. The values of a and b are $19.4 \pm 0.39 \times 10^{-4} \text{ s}^{-1}$ and $34.1 \pm 0.64 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ respectively ($r^2 = 0.9986$). Therefore, the experimental rate law has the following form:

$$\text{Rate} = k_2 [\text{PDC}] [\text{sulfide}] + k_3 [\text{PDC}] [\text{sulfide}] [\text{TsOH}] \quad (2)$$

Table 2. Dependence of the reaction rate on hydrogen-ion concentration.

	[Sulfide] = 1.00 mol dm ⁻³ ;		[PDC] = 0.001 mol dm ⁻³ ;		Temp. = 298 K	
[H ⁺]/mol dm ⁻³	0.10	0.20	0.40	0.60	0.80	1.00
k _{Obs}	23.4	27.0	33.3	39.6	47.7	54.0

3.4 Effect of substituents:

The rates of oxidation of a number of ortho-, meta- and para-substituted phenyl methyl sulfides, alkyl phenyl sulfides, dialkyl sulfides and diphenyl sulfide were determined at different temperatures and the activation parameters were calculated (Table 3). The log k_2 at different temperature is linearly related to the inverse of the absolute temperature in all cases (Figure 2). The Arrhenius equation is, therefore, valid for these oxidations.

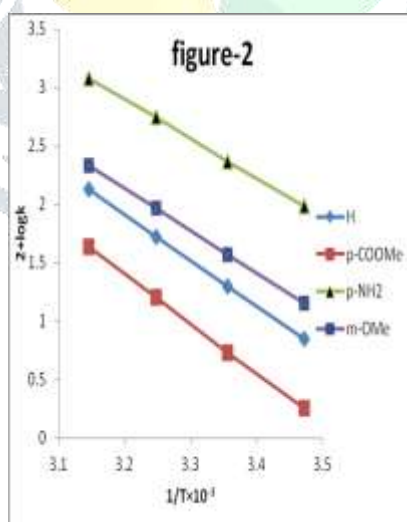


Figure 2. – Oxidation of sulfides by PDC: Effect of temperature

Table 3. Rate constants for the decomposition of PDC–Sulfides complexes and activation parameters

Subst.	$10^4 k_2 (\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$				ΔH^* kJ mol ⁻¹	$-\Delta S^*$ J mol ⁻¹ K ⁻¹	ΔG^* kJ mol ⁻¹
	288 K	298 K	308 K	318 K			
H	7.11	19.8	53.1	135	72.3±0.3	55 ± 1	88.4±0.2

p-Me	14.4	37.8	98.1	234	68.4±0.4	62±1	86.8±0.3
p-Ome	30.6	79.2	198	477	67.2±0.4	60±1	84.9±0.3
p-F	7.56	21.6	59.4	153	73.9±0.2	49±1	88.2±0.2
p-Cl	5.13	15.3	42.3	110	75.2±0.2	47±1	89.1±0.1
p-NO ₂	0.54	1.89	5.85	17.1	85.0±0.3	32±1	94.3±0.2
p-COMe	1.26	3.96	11.7	32.4	79.9±0.1	43±1	92.4±0.1
p-COOMe	1.80	5.40	16.2	43.2	78.4±0.5	45±2	91.6±0.4
p-Br	5.04	14.4	41.4	108	75.5±0.5	46±2	89.2±0.4
p-NHAc	16.2	43.2	117	270	69.3±0.7	58±2	86.4±0.5
p-NH ₂	96.3	234	558	1210	61.9±0.3	69±1	82.3±0.2
m-Me	12.6	33.3	85.5	207	68.6±0.3	63±1	87.1±0.3
m-Ome	14.4	36.9	92.7	216	66.3±0.3	69±1	86.9±0.2
m-Cl	2.79	7.92	22.5	58.5	74.9±0.5	53±2	90.6±0.4
m-Br	2.70	7.83	21.6	57.6	75.1±0.4	53±1	90.7±0.3
m-I	3.15	9.09	25.2	64.8	74.3±0.3	54±1	90.3±0.2
m-NO ₂	0.35	1.17	3.60	10.8	84.4±0.4	38±1	95.4±0.3
m-CO ₂ Me	1.44	4.41	12.6	35.1	78.4±0.4	47±1	92.1±0.3
o-Me	3.24	9.68	27.9	75.6	76.6±0.1	43±1	89.4±0.1
o-Ome	8.28	23.4	63.0	162	73.4±0.1	48±1	87.5±0.1
o-NO ₂	0.22	0.72	2.34	7.56	89.7±0.5	22±2	96.1±0.4
o-COOMe	0.45	1.53	4.86	14.4	85.8±0.2	28±1	94.0±0.2
o-Cl	0.90	3.06	9.54	27.9	83.4±0.5	30±3	92.2±0.6
o-Br	0.71	2.34	7.47	22.5	84.9±0.7	26±2	92.6±0.5
o-I	0.54	1.89	6.03	18.0	86.4±0.3	23±1	93.1±0.2
o-NH ₂	24.3	66.6	162	396	68.1±0.1	57±1	84.9±0.1

(ii) Alkyl phenyl sulfides

Et	10.8	31.5	83.7	207	72.4±0.3	51±1	87.3±0.2
Pr	7.65	22.7	63.9	162	75.1±0.2	44±1	88.1±0.2
i-Pr	9.81	28.8	82.8	216	76.1±0.3	39±1	87.5±0.2
t-Bu	3.15	9.63	29.7	74.7	78.4±0.9	40±3	90.2±0.7

(iii) Other sulfides

Me ₂ S	15.3	37.8	95.4	234	66.8±0.9	68±3	86.7±0.7
Pr ₂ S	23.4	56.7	144	324	64.6±0.7	72±2	85.7±0.6
Ph ₂ S	2.79	7.92	22.5	63.0	76.6±0.9	48±3	90.6±0.8

3.5 Effect of Solvent:

The oxidation of methyl phenyl sulfide was studied in nineteen different organic solvents. The choice of solvent was limited by the solubility of PDC and its reaction with primary and secondary alcohols. There was no reaction with the solvent chosen. The kinetics were similar in all the solvents. The values of K and k_2 are recorded in Table 4.

Table 4. Solvent effect on the oxidation of Me-S-Ph by PDC at 308 K

Solvents	$10^4 k_{\text{obs}}$ (s ⁻¹)	Solvents	$10^4 k_{\text{obs}}$ (s ⁻¹)
Chloroform	38.9	Toluene	6.31
1,2-Dichloroethane	30.9	Acetophenone	36.3
Dichloromethane	34.7	THF	13.8
DMSO	117	t-Butylalcohol	17.4
Acetone	25.1	1,4-Dioxane	12.3
DMF	53.1	1,2-Dimethoxyethane	7.76
Butanone	22.4	CS ₂	3.47
Nitrobenzene	42.7	Acetic Acid	14.5
Benzene	9.77	Ethyl Acetate	11.7
Cyclohexane	0.66		

There is an excellent correlation between the activation enthalpies and entropies of the oxidation of the thirty-four sulfides ($r^2 = 0.9376$), indicating the operation of a compensation effect[11]. However, a correlation between the calculated values of enthalpies and entropies is often vitiated by the experimental errors associated with them. The reaction exhibited an excellent isokinetic relationship also, as determined by Exner's method[12]. An Exner's plot between $\log k_2$ at 288 K and at 318 K was linear ($r^2 = 0.9976$, slope = 0.8211 ± 0.0081)(Figure 3). The value of isokinetic temperature evaluated from the Exner's plot is 611 ± 31 K. The linear isokinetic correlation implies that all the sulfides are oxidized by the same mechanism and the change in the rate of oxidation is governed by changes in both the enthalpy and entropy of the activation.

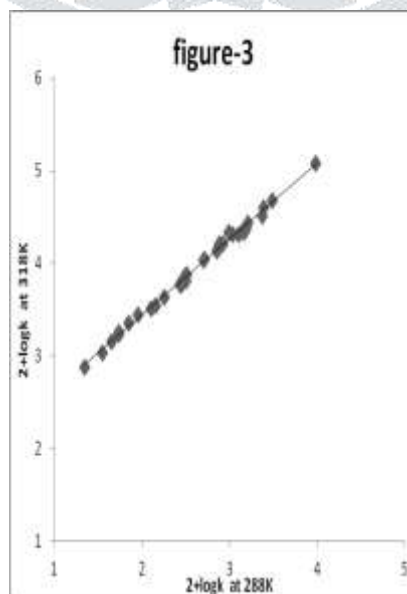


Figure 3. – Exner's Isokinetic Relationship in the oxidation of Sulphides by PDC

3.6 Solvent Effect:

The rate constants for oxidation, k_2 , in eighteen solvents (CS_2 was not considered, as the complete range of solvent parameters was not available) were correlated in terms of the linear solvation energy relationship (3) of Kamlet et al[13].

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha \quad (3)$$

In this equation, π^* represents the solvent polarity, β the hydrogen bond acceptor basicities and α is the hydrogen bond donor acidity. A_0 is the intercept term. It may be mentioned here that out of the 18 solvents, 13 have a value of zero for α . The results of correlation analyses in terms of equation (3), a biparametric equation involving π^* and β , and separately with π^* and β are given below in equation (4) - (7). We have used the standard deviation (sd), the coefficient of multiple determination (R^2), and Exner's[14] parameter, ψ , as the measures of goodness of fit. Here n is the number of data points.

$$\log k_2 = -4.07 + 1.86 (\pm 0.20) \pi^* + 0.19 (\pm 0.16) \beta + 0.30 (\pm 0.16) \alpha \quad (4)$$

$$R^2 = 0.8803; \text{ sd} = 0.18; n = 18; \psi = 0.38$$

$$\log k_2 = -4.01 + 1.75 (\pm 0.21) \pi^* + 0.29 (\pm 0.17) \beta \quad (5)$$

$$R^2 = 0.8496; \text{ sd} = 0.20; n = 18; \psi = 0.41$$

$$\log k_2 = -4.06 + 1.83 (\pm 0.21) \pi^* \quad (6)$$

$$r^2 = 0.8200; \text{ sd} = 0.19; n = 18; \psi = 0.44$$

$$\log k_2 = -2.93 + 0.61 (\pm 0.39) \beta \quad (7)$$

$$r^2 = 0.1337; \text{ sd} = 0.46; n = 18; \psi = 0.96$$

Kamlet's[13] triparametric equation explains ca. 88% of the effect of solvent on the oxidation. However, by Exner's criterion the correlation is not even satisfactory (cf. eq. 4). The major contribution is of solvent polarity. It alone accounted for ca. 82% of the data. Both β and α play relatively minor roles.

The data on the solvent effect were analysed in terms of Swain's equation[15] of cation- and anion-solvating concept of the solvents as well.

$$\log k_2 = aA + bB + C \quad (8)$$

Here A represents the anion-solvating power of the solvent and B the cation- solvating power. C is the intercept term. The rates in different solvents were analysed in terms of equation (8), separately with A and B and with (A + B).

$$\log k_2 = 1.33 (\pm 0.05) A + 1.74 (\pm 0.04) B - 3.72 \quad (9)$$

$$R^2 = 0.9942; \text{ sd} = 0.04; n = 19; \psi = 0.08$$

$$\log k_2 = 1.08 (\pm 0.06) A - 3.09 \quad (10)$$

$$r^2 = 0.1733; \text{ sd} = 0.46; n = 19; \psi = 0.93$$

$$\log k_2 = 1.64 (\pm 0.24) B - 3.84 \quad (11)$$

$$r^2 = 0.7358; \text{ sd} = 0.26; n = 19; \psi = 0.53$$

$$\log k_2 = 1.60 \pm 0.06 (A + B) - 3.73 \quad (12)$$

$$r^2 = 0.9768; \text{ sd} = 0.08; n = 19; \psi = 0.16$$

The rates of oxidation of methyl phenyl sulfide in the different solvents show an excellent correlation with Swain's equation with both the cation- and anion- solvating powers playing significant roles, though the contribution of the cation-solvation is slightly more than that of the anion-solvation. However, the correlations individually with A and B were poor. In view of the fact that solvent polarity is able to account for ca. 98% of the data, an attempt was made to correlate the rate with the relative permittivity of the solvent. However, a plot of $\log k_2$ against the inverse of the relative permittivity is not linear ($r^2 = 0.4962$; $\text{sd} = 0.36$; $\psi = 0.73$).

3.7 Correlation Analysis of Reactivity

The data in Table 3 show that the oxidation of different sulfides follows the order of their nucleophilicity: $\text{Pr}_2\text{S} > \text{Me}_2\text{S} > \text{MeSPh} > \text{Ph}_2\text{S}$.

3.7.1 Aryl Methyl Sulfides

The correlation of the effect of substituents on the reactivity has been widely attempted in terms of the Hammett equation[16] or with dual substituent-parameter equations[17,18]. In the late 1980s, Charton[19] introduced a triparametric LDR equation for the quantitative description of structural effects on chemical reactivities. This triparametric equation results from the fact that substituent types differ in their mode of electron delocalization. This difference is reflected in a different sensitivity to the electronic demand for the phenomenon being studied. It has the advantage of not requiring a choice of parameters as the same three substituent constants are reported to cover the entire range of electrical effects of substituents. We have, therefore, begun a study of structural effects on reactivity by means of the LDR equation. In this work, we have applied the LDR equation (13) to the rate constants, k_2 .

$$\log k_2 = L \sigma_1 + D \sigma_d + R \sigma_e + h \quad (13)$$

Here, σ_1 is a localized (field and/or inductive) effect parameter, σ_d is the intrinsic delocalized (resonance) electrical effect

parameter when active site electronic demand is minimal and σ_e represents the sensitivity of the substituent to changes in electronic demand by the active site. The latter two substituent parameters are related by equation (14).

$$\sigma_D = \eta\sigma_e + \sigma_d \quad (14)$$

Here η represents the electronic demand of the reaction site and represents the ratio of regression coefficient of the sensitivity parameter, σ_e and that of resonance parameter, σ_d i.e. $\eta = R/D$. σ_D represents the delocalized electrical parameter of the diparametric LD equation.

For ortho-substituted compounds, it is necessary to account for the possibility of steric effects and Charton¹⁹ therefore, modified the LDR equation to generate the LDRS equation (15).

$$\log k_2 = L\sigma_1 + D\sigma_d + R\sigma_e + S\upsilon + h \quad (15)$$

Where υ is the well-known Charton's steric parameter based on Van der Waals radii[20].

The rates of oxidation of ortho-, meta- and para-substituted sulfides show excellent correlations in terms of the LDR/LDRS equations. The values of the independent variables, σ_1 , σ_d , σ_e and υ , were obtained from the work of Charton and Charton¹⁹. Though the number of data-points is less than the optimum number, the correlations are excellent as per Exner's¹² criterion also. Exner's Ψ parameter takes into account the number of data-point also.

All three regression coefficients, L, D and R, are negative indicating an electron-deficient sulfur center in the transition state of the rate-determining step. The positive value of η adds a negative increment to σ_d as in equation (15), increasing the electron-donating power of the substituent and its capacity to stabilize a cationic species.

The negative value of S indicates that the reaction is subjected to steric hindrance by the ortho-substituent. This may be due to steric hindrance of the ortho-substituent to the approach of the oxidizing species.

To test the significance of localized, delocalized and steric effects in the ortho-substituted sulfides, multiple linear regression analyses were carried out with (i) σ_1 , σ_d and σ_e , (ii) σ_d , σ_e and υ , and (iii) σ_1 , σ_e and υ . The absence of significant correlations [eqns. (16)-(18)] showed that all the four substituent constants are significant.

$$\log k_2 = -1.87 (\pm 0.43)\sigma_1 - 1.24 (\pm 0.35)\sigma_d - 1.92 (\pm 2.50)\sigma_e - 3.02 \quad (16)$$

$$R^2 = 0.8973, \quad sd = 0.27, \quad n = 10, \quad \Psi = 0.39$$

$$\log k_2 = -1.76 (\pm 0.42)\sigma_d + 0.44 (\pm 0.29)\sigma_e - 1.70 (\pm 0.51)\upsilon - 2.82 \quad (17)$$

$$R^2 = 0.8486, \quad sd = 0.32, \quad n = 10, \quad \Psi = 0.48$$

$$\log k_2 = -1.99 (\pm 0.82)\sigma_1 - 5.08 (\pm 4.09)\sigma_e - 0.64 (\pm 0.82)\upsilon - 2.61 \quad (18)$$

$$R^2 = 0.6843, \quad sd = 0.47, \quad n = 10, \quad \Psi = 0.69$$

Similarly in the cases of the oxidation of para- and meta-substituted sulfides, multiple regression analyses indicated that both localization and delocalization effects are significant. There is no significant collinearity between the various substituent constants for the three series.

The percent contribution[20] of the delocalized effect, P_D is given by the following equation (19).

$$P_D = (|D| \times 100) / (|L| + |D| + |R|) \quad (19)$$

Similarly, the percent contribution of the steric parameter²⁰ to the total effect of the substituent, P_S , was determined by using equation (20).

$$P_S = (|S| \times 100) / (|L| + |D| + |S| + |R|) \quad (20)$$

The values of P_D and P_S are also recorded in Table 5. The value of P_D for the oxidation of para-substituted sulfides is ca. 38% whereas the corresponding values for the meta- and ortho-substituted aldehydes are ca. 33 and 37% respectively. The less pronounced resonance effect from the ortho-position than from the para-position may be due to the twisting away of the methyl-thio group from the plane of the benzene ring.

Table 5. Temperature dependence for the reaction constants for the oxidation of organic sulfides by PDC

T/K	-L	-D	-R	-S	η	R ²	sd	ψ	P _D	P _S
Para-substituted										
288	1.38	1.72	1.49	-	0.87	0.9999	0.006	0.01	37.4	-
298	1.25	1.62	1.43	-	0.88	0.9989	0.006	0.02	37.7	-
308	1.17	1.53	1.37	-	0.89	0.9998	0.007	0.01	37.6	-
318	1.08	1.44	1.20	-	0.83	0.9999	0.004	0.02	38.7	-
Meta-substituted										
288	1.72	1.36	1.07	-	0.79	0.9999	0.005	0.01	32.8	-
298	1.62	1.26	1.01	-	0.80	0.9989	0.003	0.02	32.4	-
308	1.52	1.18	0.81	-	0.69	0.9998	0.006	0.02	33.6	-
318	1.43	1.07	0.66	-	0.62	0.9999	0.002	0.01	33.9	-
Ortho-substituted										
288	1.41	1.49	1.38	1.20	0.93	0.9998	0.014	0.02	34.8	21.9
298	1.34	1.43	1.25	1.08	0.87	0.9999	0.002	0.01	35.6	21.2
308	1.26	1.34	0.99	0.98	0.74	0.9989	0.002	0.04	37.3	21.4
318	1.16	1.27	0.92	0.92	0.72	0.9999	0.005	0.01	38.9	21.5

In earlier studies on the oxidations of sulfides, involving a direct oxygen transfer *via* an electrophilic attack on the sulfide-sulfur, the reaction constants were negative but of relatively small magnitude, e.g. by hydrogen peroxide (-1.13)[21], periodate (-1.40)[22], permanganate (-1.52)[23], and peroxydisulfate (-0.56)[24]. Large negative reaction constants were exhibited by oxidations involving formation of halogeno-sulfonium cations e.g. by chloramine-T(-4.25)[25], bromine (-3.2)[26] and N-bromoacetamide (-3.75)[27]. In the oxidation by N-chloroacetamide (NCA)[28] the values of field (ρ_f) and resonance (ρ_R^+), at 298 K are -1.3 and -1.7 respectively.

3.7.2 Alkyl Phenyl Sulfides

The rates of oxidation of alkyl phenyl sulfides did not yield any significant correlation separately with Taft's σ^* or E_s values. The rates were therefore analysed in terms of Pavelich-Taft's[29] dual substituent-parameter (DSP) equation (21).

$$\log k_2 = \rho^* \sigma^* + \delta E_s + \log k_0 \quad (21)$$

The correlations are excellent (Table 6). Though the number of compounds is small (five) for any analysis by a DSP equation, the results can be used qualitatively. The negative polar reaction constant confirms that the electron-donating power of the alkyl group enhances the reaction rate. The steric effect plays a minor inhibitory role.

Table 6. Correlation of rate of oxidation of alkyl phenyl sulfides with Pavelich-Taft equation^a

Temp./K	$-\rho^*$	δ	R ²	Sd	ψ
288	2.44±0.01	0.70±0.01	0.9987	0.011	0.05
298	2.57±0.01	0.70±0.01	0.9982	0.012	0.05
308	2.62±0.02	0.67±0.01	0.9938	0.021	0.10
318	2.67±0.03	0.68±0.02	0.9872	0.030	0.15

^a No. of data points = 5

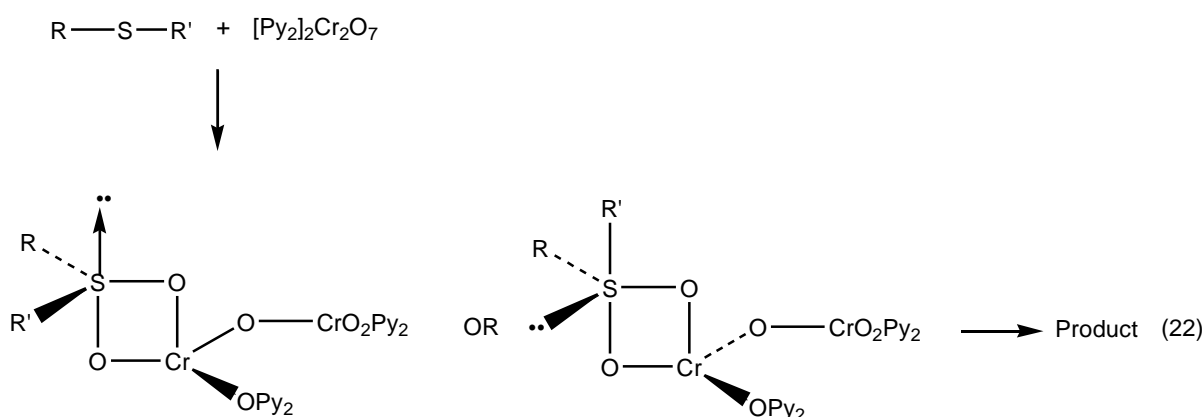
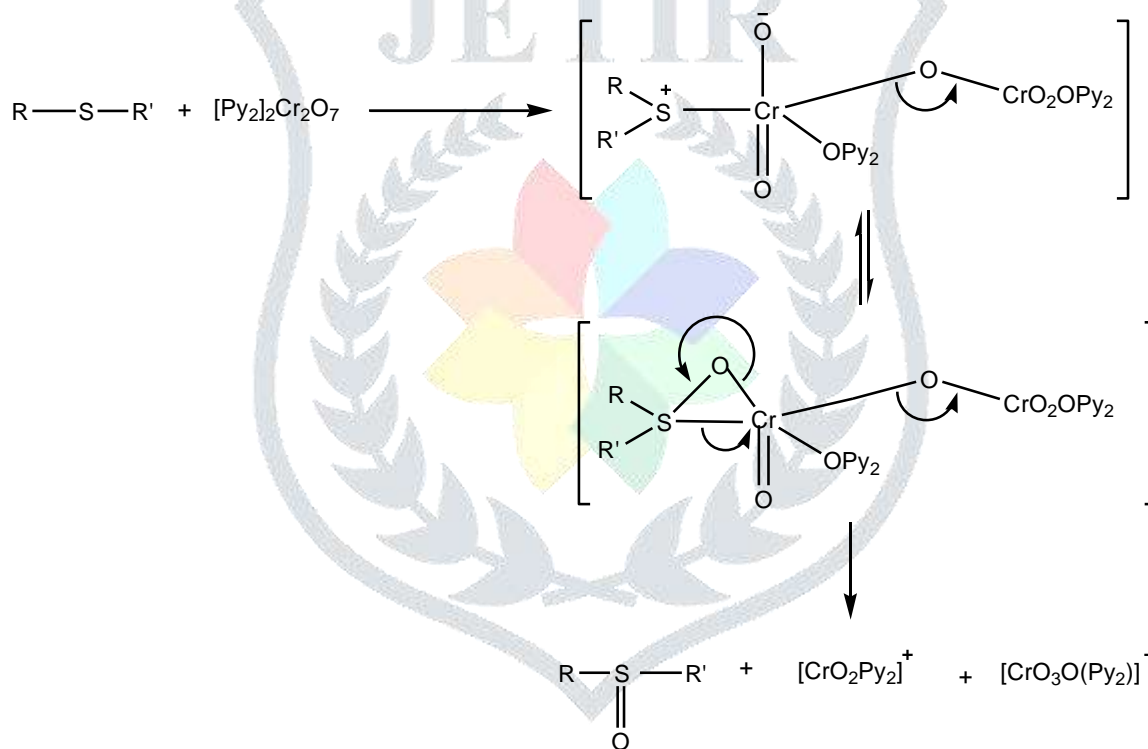
4. MECHANISMS:

In view of the absence of any effect of radical scavenger, acrylonitrile, on the reaction rate, it is unlikely that a one electron reaction giving rise to free radicals, is operative in this oxidation. The observed Michaelis-Menten kinetics with respect to sulfides led us to suggest the formation of a 1:1 complex of PDC and sulfides in a rapid pre-equilibrium. With present set of data, it is difficult to state the definite nature of the intermediate complex. Theoretical calculations[30] have shown that there is a substantial charge transfer from the metal to the oxygen in dichromate. The most logical mode of interaction between sulfides and PDC would, therefore be nucleophilic attack at the metal. Donation of a unshared pair of electrons to an empty d-orbital on the metal would result in the formation of a coordinate covalent bond. The initial formed intermediate is likely to undergo a further rapid reaction in which the incipient oxide and sulfonium ions bond to form a highly structured intermediate, that would rearrange to give a sulfoxide (Scheme 1).

The oxidation of sulfides by PDC may involve a cyclic intermediate as has been suggested in many reactions of Cr(VI). The cyclic transition state will be highly strained in view of the apical position of a lone pair of electrons or an alkyl group (22). The steric requirements of the reaction (22) will be higher as compared to those of reaction of Scheme 1 and the observed small magnitudes of steric reaction constants are thus consistent with the proposed acyclic mechanism. The formation of a cyclic transition state entails a more exacting specificity of orientation and should result in much larger negative entropy of activation than that observed.

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