

Kinetics and mechanism of the oxidation of organic sulphides by 2,2'-bipyridinium chlorochromate

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Abstract. The oxidation of 34 organic sulphides by 2,2'-bipyridinium chlorochromate (BPCC) resulted in the formation of the corresponding sulphoxides. The reaction is first order with respect to both BPCC and the sulphide, and is catalysed by hydrogen ions. The hydrogen-ion dependence has the form: $k_{\text{obs}} = a + b[\text{H}^+]$. The oxidation was studied in 19 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 rates of oxidation meta- and *p*-substituted phenyl methyl sulphides were correlated with Charton's LDR equation. The rates of the *o*-compounds showed excellent correlation with the LDRS equation. Oxidation of the *p*-compounds is more susceptible to the delocalization effect. Oxidation of the *m*-compounds exhibited a greater dependence on the field effect. In the oxidation of the *o*-compounds, the contribution of delocalized effect is slightly more than that of the field effect. The oxidation of alkyl phenyl sulphides is subject to both polar and steric effects of the alkyl groups. Polar reaction constants are negative, indicating an electron-deficient sulphur centre in the rate-determining step. A mechanism involving formation of a sulphurane intermediate in the slow step has been proposed.

Keywords. Correlation analysis; halochromates; organic sulphides.

1. Introduction

2,2'-Bipyridinium chlorochromate (BPCC), has been used as an mild and selective oxidant in synthetic organic chemistry¹. There are only a few reports about the kinetics and mechanism of oxidation by BPCC, available in the literature²⁻⁵, while the kinetics of oxidation of organic sulphides by BPCC has not been investigated. We have been interested in the study of kinetics and mechanism of reactions of complexed Cr(VI) species and have already reported the kinetics of oxidation of sulphides by pyridinium fluoro- and bromo-chromates^{6,7}. Recently Karunakaran *et al*⁸ have given a common mechanism for the oxidation of diphenyl sulphide by Cr(VI) reagent in acetic acid. In the present article, we report the kinetics of oxidation of thirty-four organic sulphides by BPCC in dimethylsulphoxide (DMSO) as solvent. Attempts have been made to correlate rate and structure in this reaction. A probable mechanism has been proposed.

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2. Experimental

2.1 Materials

The sulphides were either commercial products or prepared by known methods⁹⁻¹⁵ 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. BPCC was prepared by the reported method¹. Toluene-*p*-sulphonic acid was used as the source of hydrogen ions.

2.2 Product analysis

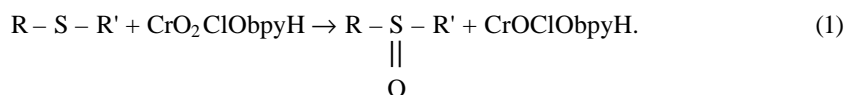
MeSPh or Me₂S (0.01 mol) and BPCC (0.01 mol) was dissolved in DMSO (50 ml) and the mixture was allowed to stand for about 20 h. Most of the solvent was removed under reduced pressure. The residue was diluted with water and extracted with chloroform (3 × 50 ml). The chloroform layer was dried over anhydrous magnesium sulphate, 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 sulphoxides. Peaks characteristic of sulphide and sulphone 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 sulphones¹⁶ was seen. In NMR spectroscopy, studied in the case of Me₂S, the peak due to methyl protons shifted from 2.1 τ in the sulphide, to 2.6 τ in the product. In the corresponding sulphone, the peak should have appeared at 3.0 τ ¹⁷. Similar experiments were performed with the other sulphides also. In all cases, the products were the corresponding sulphoxides. The oxidation state of chromium in completely reduced reaction mixtures, determined by the iodometric method, was 3.92 ± 0.15.

2.3 Kinetic measurements

The reactions were studied under pseudo-first-order conditions by keeping an excess (× 15 or greater) of the sulphide over BPCC. The solvent was DMSO, unless mentioned otherwise. The reactions were studied at constant temperature (± 0.1 K) and were followed by monitoring the decrease in the concentration of BPCC at 365 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 [BPCC] against time. Duplicate kinetic runs showed that the rate constants are reproducible to within ± 3%. The values of the second order rate constants were computed from the relation *k*₂ = *k*_{obs}/[sulphide]. Simple and multivariate regression analyses were carried out by the least-squares method.

3. Results

The oxidation of organic sulphides by BPCC resulted in the formation of the corresponding sulphoxides. The overall reaction may be represented as,



BPCC undergoes a two-electron change. This is in accord to our earlier observations with other halochromates^{6,7} and BPCC^{4,5}.

3.1 Rate laws

The reactions were found to be first order with respect to BPCC. Individual kinetic runs were strictly first order with respect to BPCC. Further, the first-order rate coefficients did not vary with the initial concentration of BPCC. The order with respect to sulphide also was found to be one (table 1).

3.2 Induced polymerization of acrylonitrile

The oxidation of methyl phenyl sulphide, 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).

3.3 Effect of substituents

The rates of oxidation of a number of *o*-, *m*- and *p*-substituted phenyl methyl sulphides, alkyl phenyl sulphides, dialkyl sulphides and diphenyl sulphide were determined at different temperatures and the activation parameters were calculated (table 2).

3.4 Effect of acidity

The reaction is catalysed by hydrogen ions (table 3). The hydrogen-ion dependence has the form $k_{\text{obs}} = a + b [\text{H}^+]$ (table 3). The values of a and b are $1.75 \pm 0.04 \times 10^{-5} \text{ s}^{-1}$ and $3.09 \pm 0.06 \times 10^{-5} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ respectively ($r^2 = 0.9985$).

3.5 Effect of solvent

The oxidation of methyl phenyl sulphide was studied in nineteen different organic solvents. The choice of solvent was limited by the solubility of BPCC and its reaction

Table 1. Rate constants for the oxidation of methyl phenyl sulphide by BPCC at 303 K.

$10^3[\text{BPCC}] (\text{mol dm}^{-3})$	$[\text{MeSPh}] (\text{mol dm}^{-3})$	$10^6 k_{\text{obs}} (\text{s}^{-1})$
1.0	0.10	17.6
1.0	0.20	34.8
1.0	0.40	70.1
1.0	0.60	105
1.0	0.80	141
1.0	1.00	174
2.0	0.20	34.0
4.0	0.20	35.5
6.0	0.20	34.6
8.0	0.20	35.1
1.0	0.40*	71.4*

*Contained $0.001 \text{ mol dm}^{-3}$ acrylonitrile

Table 2. Rate constants and activation parameters of the oxidation of organic sulphides by BPCC.

Substituent	$10^5 k_2$ (dm ³ mol ⁻¹ s ⁻¹) at				ΔH^* (kJ mol ⁻¹)	ΔS^* (J mol ⁻¹ K ⁻¹)	ΔG^* (kJ mol ⁻¹)
	293 K	303 K	313 K	323 K			
(i) <i>Phenyl methyl sulphides</i>							
H	6.58	17.4	45.3	118	73.1 ± 0.9	-76 ± 3	95.6 ± 0.7
<i>p</i> -Me	12.8	32.6	83.0	207	70.5 ± 0.8	-80 ± 2	94.0 ± 0.6
<i>p</i> -OMe	26.4	66.0	160	398	68.4 ± 0.9	-81 ± 3	92.3 ± 0.8
<i>p</i> -F	6.81	18.3	48.1	127	74.1 ± 0.9	-73 ± 3	95.5 ± 0.8
<i>p</i> -Cl	4.74	13.0	34.0	91.2	74.8 ± 0.9	-73 ± 3	96.4 ± 0.7
<i>p</i> -NO ₂	0.55	1.66	4.79	14.0	82.2 ± 0.9	-66 ± 3	101 ± 0.7
<i>p</i> -COMe	1.23	3.53	9.84	27.1	78.5 ± 0.8	-72 ± 3	99.7 ± 0.6
<i>p</i> -COOMe	1.69	4.81	13.2	36.2	77.7 ± 0.8	-72 ± 3	98.9 ± 0.6
<i>p</i> -Br	4.60	12.6	33.1	90.0	75.6 ± 0.9	-71 ± 3	96.5 ± 0.7
<i>p</i> -NHAc	14.0	36.6	91.1	228	70.6 ± 0.8	-78 ± 2	93.8 ± 0.6
<i>p</i> -NH ₂	77.6	189	448	1050	65.7 ± 0.6	-81 ± 2	89.6 ± 0.5
<i>m</i> -Me	11.6	30.3	76.0	184	69.9 ± 0.3	-82 ± 1	94.3 ± 0.3
<i>m</i> -OMe	13.3	34.0	85.6	203	69.1 ± 0.4	-84 ± 1	93.9 ± 0.3
<i>m</i> -Cl	2.55	6.97	18.6	50.0	75.4 ± 0.9	-76 ± 3	97.9 ± 0.7
<i>m</i> -Br	2.47	6.74	18.1	48.6	75.5 ± 0.9	-76 ± 3	98.0 ± 0.7
<i>m</i> -I	2.96	8.05	21.0	55.4	74.1 ± 0.8	-79 ± 3	97.6 ± 0.6
<i>m</i> -NO ₂	0.31	0.96	2.85	8.10	83.0 ± 0.4	-68 ± 1	103 ± 0.4
<i>m</i> -CO ₂ Me	1.36	3.82	10.6	28.1	77.0 ± 0.6	-76 ± 2	99.5 ± 0.5
<i>o</i> -Me	3.19	8.96	24.2	64.7	76.3 ± 0.7	-71 ± 2	97.4 ± 0.6
<i>o</i> -OMe	8.55	22.0	56.6	143	71.4 ± 0.9	-80 ± 3	95.0 ± 0.7
<i>o</i> -NO ₂	0.18	0.57	1.79	5.60	87.6 ± 1.0	-57 ± 4	104 ± 0.9
<i>o</i> -COOMe	0.43	1.30	3.88	11.8	84.2 ± 1.0	-61 ± 4	102 ± 0.9
<i>o</i> -Cl	0.92	2.72	7.80	23.3	79.7 ± 0.6	-69 ± 2	100 ± 0.4
<i>o</i> -Br	0.69	2.10	6.12	16.8	81.2 ± 0.4	-67 ± 1	101 ± 0.3
<i>o</i> -I	0.53	1.68	4.98	14.1	83.5 ± 0.2	-62 ± 1	102 ± 0.2
<i>o</i> -NH ₂	23.0	63.7	152	386	70.9 ± 0.8	-73 ± 3	92.5 ± 0.6
(ii) <i>Alkyl phenyl sulphides</i>							
Et	10.3	26.6	67.4	168	70.7 ± 0.7	-81 ± 2	94.6 ± 0.5
Pr	6.89	18.5	47.9	122	72.8 ± 0.6	-77 ± 2	95.5 ± 0.5
<i>i</i> -Pr	8.68	23.0	59.4	151	72.3 ± 0.7	-77 ± 2	95.0 ± 0.6
<i>t</i> -Bu	2.66	8.16	22.2	63.2	80.1 ± 0.8	-60 ± 3	97.7 ± 0.7
(iii) <i>Other sulphides</i>							
Me ₂ S	21.1	53.6	131	322	68.8 ± 0.7	-81 ± 2	92.8 ± 0.6
Pr ₂ S	33.4	82.2	208	512	69.2 ± 1.0	-76 ± 3	91.7 ± 0.8
Ph ₂ S	4.04	11.6	33.2	91.3	79.3 ± 0.8	-69 ± 3	96.7 ± 0.6

Table 3. Dependence of the reaction rate on hydrogen-ion concentration.

[MeSPh] 0.10 mol dm ⁻³	[BPCC] 0.001 mol dm ⁻³	Temp. 303 K				
[TsOH] (mol dm ⁻³)	0.10	0.20	0.40	0.60	0.80	1.00
$10^6 k_{\text{obs}}$ (s ⁻¹)	20.6	24.1	29.8	35.3	42.2	48.8

Table 4. Solvent effect on the oxidation of MeSPh by BPCC at 303 K.

Solvent	$10^6 k_2$ (s ⁻¹)	Solvent	$10^6 k_2$ (s ⁻¹)
Chloroform	57.5	Toluene	10.2
1,2-Dichloroethane	53.7	Acetophenone	61.6
Dichloromethane	50.1	Tetrahydrofuran	18.6
Dimethyl sulphoxide	174	<i>t</i> -Butyl alcohol	24.0
Acetone	40.7	1,4-Dioxane	21.4
DMF	79.4	1,2-Dimethoxyethane	11.7
Butanone	33.9	Ethyl acetate	15.8
Nitrobenzene	64.6	Carbon disulphide	5.37
Benzene	13.8	Acetic acid	26.3
Cyclohexane	1.12		

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_2 are recorded in table 4.

4. Discussion

Correlation of the entropies and enthalpies of activation of the oxidation of thirty-four sulphides is satisfactory ($r^2 = 0.9569$). The value of the isokinetic temperature is 915 ± 85 K. The correlation was tested and found genuine by Exner's¹⁸ method. Exner has suggested an alternative method of testing the validity of isokinetic relationship. A plot between $\log k_2$ at 293 K and at 323 K was linear (slope = 0.8634 ± 0.01 ; $r^2 = 0.9991$). The value of the isokinetic temperature, calculated by Exner's method, is 925 ± 96 K, which is in fair agreement with the value obtained earlier. A linear isokinetic relationship is a necessary condition for the validity of linear free energy relationships. It also implies that all the compounds so correlated react by the same mechanism¹⁸.

4.1 Solvent effect

Rate constants for oxidation, k_2 , in eighteen solvents (CS₂ was not considered, as the complete range of solvent parameters was not available) were correlated in terms of the linear solvation energy relationship of Kamlet *et al.*,¹⁹

$$\log k_2 = A_0 + p\mathbf{p}^* + b\mathbf{b} + a\mathbf{a} \quad (2)$$

In this equation, \mathbf{p}^* represents the solvent polarity, \mathbf{b} the hydrogen bond acceptor basicities and \mathbf{a} the hydrogen bond donor acidity. A_0 is the intercept term. It may be mentioned here that out of the 18 solvents, 12 have a value of zero for \mathbf{a} . The results of correlation analyses in terms of (2), a biparametric equation involving \mathbf{p}^* and \mathbf{b} and separately with \mathbf{p}^* and \mathbf{b} are given below in (3)–(6).

$$\log k_2 = -5.87 + 1.87 (\pm 0.19)\mathbf{p}^* + 0.14 (\pm 0.15)\mathbf{b} + 0.34 (\pm 0.15)\mathbf{a} \quad (3)$$

$$R^2 = 0.8946, \text{sd} = 0.17, n = 18, \mathbf{y} = 0.25,$$

$$\log k_2 = -5.79 + 1.75 (\pm 0.20)\mathbf{p}^* + 0.25 (\pm 0.17)\mathbf{b} \quad (4)$$

$$R^2 = 0.8541, \text{sd} = 0.19, n = 18, \mathbf{y} = 0.29,$$

$$\log k_2 = -5.74 + 1.82 (\pm 0.20) \mathbf{P}^*, \quad (5)$$

$$r^2 = 0.8312, \text{ sd} = 0.20, n = 18, \mathbf{y} = 0.31,$$

$$\log k_2 = -4.77 + 0.57 (\pm 0.38) \mathbf{b} \quad (6)$$

$$r^2 = 0.1203, \text{ sd} = 0.83, n = 18, \mathbf{y} = 0.83.$$

Here n is the number of data points and \mathbf{y} is Exner's statistical parameter²⁰.

Kamlet's¹⁹ triparametric equation explains $\approx 89\%$ of the effect of solvent on the oxidation. However, by Exner's criterion the correlation is not even satisfactory (cf. (3)). The major contribution is of solvent polarity. It alone accounted for $\approx 83\%$ of the data. Both \mathbf{b} and \mathbf{a} play relatively minor roles.

Data on the solvent effect were analysed in terms of Swain's equation²¹ of cation- and anion-solvating concept of the solvents as well,

$$\log k_2 = aA + bB + C. \quad (7)$$

Here A represents the anion-solvating power of the solvent and B the cation-solvating power, C is the intercept term, $(A + B)$ represents the solvent polarity. The rates in different solvents were analysed in terms of (7), separately with A and B and with $(A + B)$.

$$\log k_2 = 1.37 (\pm 0.03)A + 1.70 (\pm 0.02)B - 6.08, \quad (8)$$

$$R^2 = 0.9983, \text{ sd} = 0.02, n = 19, \mathbf{y} = 0.03,$$

$$\log k_2 = 1.13 (\pm 0.56)A - 4.91, \quad (9)$$

$$r^2 = 0.1917, \text{ sd} = 0.45, n = 19, \mathbf{y} = 0.77,$$

$$\log k_2 = 1.60 (\pm 0.24)B - 5.63, \quad (10)$$

$$r^2 = 0.7186, \text{ sd} = 0.27, n = 19, \mathbf{y} = 0.40,$$

$$\log k_2 = 1.59 \pm 0.05 (A + B) - 6.07, \quad (11)$$

$$r^2 = 0.9863, \text{ sd} = 0.06; n = 19, \mathbf{y} = 0.09.$$

The rates of oxidation of methyl phenyl sulphide in the different solvents show excellent correlation with Swain's equation with both the cation- and anion-solvating powers playing significant roles, though the contribution of cation-solvation is slightly more than that of anion-solvation. The solvent polarity, represented by $(A + B)$, also accounted for $\approx 99\%$ of the data. However, the correlations with A and B individually were poor. In view of the fact that solvent polarity is able to account for $\approx 99\%$ 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 ($r^2 = 0.5983$, $\text{sd} = 0.32$, $\mathbf{y} = 0.49$).

4.2 Correlation analysis of reactivity

The data in table 2 show that the oxidation of different sulphides follows the order of their nucleophilicity: $\text{Pr}_2\text{S} > \text{Me}_2\text{S} > \text{MeSPh} > \text{Ph}_2\text{S}$.

4.2a *Aryl methyl sulphides*: The correlation of the effect of substituents on the reactivity has been widely attempted in terms of the Hammett equation²² or with dual substituent-parameter equations^{23,24}. In the late 1980s, Charton²⁵ 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 below to the rate constants, k_2 ,

$$\log k_2 = L\mathfrak{S} + D\mathfrak{S}_i + R\mathfrak{S}_j + h. \quad (12)$$

Here, \mathfrak{S} is a localized (field and/or inductive) effect parameter, \mathfrak{S}_i is the intrinsic delocalized (resonance) electrical effect parameter when active site electronic demand is minimal and \mathfrak{S}_j represents the sensitivity of the substituent to changes in electronic demand by the active site. The latter two substituent parameters are related by,

$$\mathfrak{S}_j = h\mathfrak{S} + \mathfrak{S}_i. \quad (13)$$

Here h represents the electronic demand of the reaction site and is given by relation $h = R/D$, and \mathfrak{S}_i represents the delocalized electrical parameter of the diparametric *LD* equation.

For *o*-substituted compounds, it is necessary to account for the possibility of steric effects and Charton²⁵ therefore, modified the *LDR* equation to generate the *LDRS* equation,

$$\log k_2 = L\mathfrak{S} + D\mathfrak{S}_i + R\mathfrak{S}_j + Su + h, \quad (14)$$

where u is the well-known Charton's steric parameter based on Van der Waals radii²⁶.

The rates of oxidation of *o*-, *m*- and *p*-substituted sulphides show excellent correlations in terms of the *LDR/LDRS* equations (table 5). The values of the independent variables, \mathfrak{S} , \mathfrak{S}_i , \mathfrak{S}_j and u were obtained from the work of Charton and Charton²⁵. Though the number of data-points is less than the optimum number, the correlations are excellent as per Exner's²⁰ criterion also. Exner's y parameter takes into account the number of data-points also.

The comparison of the *L* and *D* values for the substituted sulphides showed that the oxidation of *p*-substituted sulphides is more susceptible to the delocalization effect than to the localized effect. However, the oxidation of *o*- and *m*-substituted compounds exhibited a greater dependence on the field effect. In all cases, the magnitude of the reaction constants decreases with increase in the temperature, pointing to a decrease in selectivity with increase in temperature.

All three regression coefficients, *L*, *D* and *R*, are negative indicating an electron-deficient sulphur centre in the transition state of the rate-determining step. The positive value of h adds a negative increment to \mathfrak{S}_i as in (14), reflecting the electron-donating power of the substituent and its capacity to stabilize a cationic species.

Table 5. Temperature dependence for the reaction constants for the oxidation of organic sulphides by BPCC.

$T(K)$	L	D	R	S	h	R^2	sd	y	P_D	P_S
<i>p</i> -Substituted										
293	-1.33	-1.65	-1.37	-	0.83	0.9999	0.004	0.01	55.4	-
303	-1.25	-1.58	-1.36	-	0.86	0.9998	0.003	0.02	55.8	-
313	-1.20	-1.51	-1.28	-	0.85	0.9997	0.003	0.01	55.7	-
323	-1.13	-1.45	-1.19	-	0.82	0.9998	0.004	0.01	56.2	-
<i>m</i> -Substituted										
293	-1.74	-1.37	-1.15	-	0.93	0.9999	0.007	0.01	44.1	-
303	-1.67	-1.30	-1.14	-	0.88	0.9998	0.005	0.01	43.8	-
313	-1.59	-1.24	-1.11	-	0.90	0.9999	0.005	0.02	43.8	-
323	-1.50	-1.17	-1.07	-	0.92	0.9997	0.004	0.01	43.0	-
<i>o</i> -Substituted										
293	-1.45	-1.55	-1.26	-1.13	0.81	0.9997	0.016	0.02	51.5	27.4
303	-1.40	-1.49	-1.20	-1.05	0.81	0.9999	0.002	0.01	51.6	26.6
313	-1.33	-1.41	-1.17	-0.99	0.83	0.9998	0.003	0.01	51.5	26.5
323	-1.26	-1.33	-1.10	-0.96	0.87	0.9997	0.015	0.02	51.4	27.0

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

To test the significance of localized, delocalized and steric effects in the *o*-substituted sulphides, multiple linear regression analyses were carried out with (i) \mathbf{S} , \mathbf{S}_i and \mathbf{S}_o , (ii) \mathbf{S}_i , \mathbf{S} and \mathbf{u} (iii) \mathbf{S} , \mathbf{S} and \mathbf{u} . The absence of significant correlations as depicted in (15)–(17) below, shows that all the four substituent constants are significant.

$$\log k_2 = (-1.77 \pm 0.36)\mathbf{S} - (1.20 \pm 0.29)\mathbf{S}_i - (1.80 \pm 2.14)\mathbf{S}_o - 4.64, \quad (15)$$

$$R^2 = 0.9170, \text{ sd} = 0.23, n = 10, \mathbf{y} = 0.25,$$

$$\log k_2 = (-1.85 \pm 0.37)\mathbf{S}_i + (0.89 \pm 2.79)\mathbf{S} - (1.59 \pm 0.49)\mathbf{u} - 4.49, \quad (16)$$

$$R^2 = 0.8504, \text{ sd} = 0.31, n = 10, \mathbf{y} = 0.33,$$

$$\log k_2 = (-2.14 \pm 0.69)\mathbf{S} - (4.93 \pm 3.78)\mathbf{S}_o - (0.46 \pm 0.74)\mathbf{u} - 4.27, \quad (17)$$

$$R^2 = 0.7027, \text{ sd} = 0.43, n = 10, \mathbf{y} = 0.48.$$

Similarly, in the cases of the oxidation of *p*- and *m*-substituted sulphides, 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 contribution²⁶ of the delocalized effect, P_D is given by the following,

$$P_D = (|D| \times 100) / (|L| + |D|). \quad (18)$$

Similarly, the percent contribution of the steric parameter²⁶ to the total effect of the substituent, P_S , was determined by using,

$$P_S = (|S| \times 100) / (|L| + |D| + |S|). \quad (19)$$

Values of P_D and P_S are also recorded in table 5. The value of P_D for the oxidation of *p*-substituted sulphides is $\approx 52\%$ whereas the corresponding values for the *m*- and *o*-substituted aldehydes are ≈ 39 and 49% respectively. This shows that the balance of localization and delocalization effects is different for differently substituted sulphides. The less pronounced resonance effect from the *o*-position than from the *p*-position may be due to the twisting away of the methylthio group from the plane of the benzene ring. The magnitude of the P_S value shows that the steric effect is significant in this reaction.

In earlier studies on the oxidations of sulphides, involving a direct oxygen transfer via an electrophilic attack on the sulphide-sulphur, the reaction constants were negative but of relatively small magnitude, e.g. by hydrogen peroxide (-1.13)²⁷, periodate (-1.40)²⁸, permanganate (-1.52)²⁹, and peroxydisulphate (-0.56)³⁰. Large negative reaction constants were exhibited by oxidations involving formation of halogeno-sulphonium cations, e.g. by chloramine-T (-4.25)³¹, bromine (-3.2)³² and N-bromoacetamide (-3.75)³³. In the oxidation by N-chloroacetamide (NCA)³⁴ the values of field (\mathbf{r}) and resonance (\mathbf{r}_R^+), at 298 K are -1.3 and -1.7 respectively.

4.2b *Alkyl phenyl sulphides*: The rates of oxidation of alkyl phenyl sulphides did not yield any significant correlation separately with Taft's \mathbf{S}^* or E_s values. The rates were therefore analysed in terms of Pavelich-Taft's³⁵ dual substituent-parameter (DSP) equation,

$$\log k_2 = \mathbf{r}^* \mathbf{S}^* + \mathbf{d}E_s + \log k_0. \quad (20)$$

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.

5. Mechanism

The observed hydrogen-ion dependence suggests that the reaction follows two mechanistic pathways, one acid-independent and the other acid-dependent. The acid-catalysis can be attributed to a protonation of BPCC to give a stronger oxidant and electrophile,



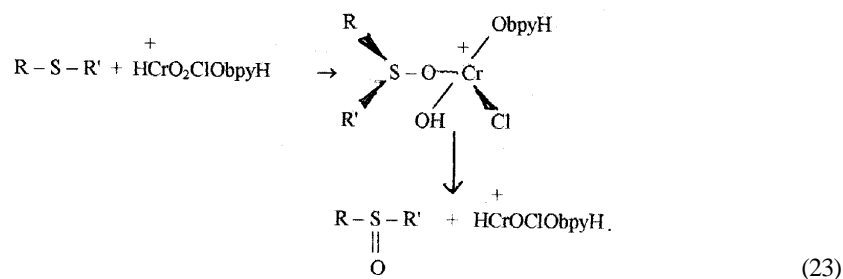
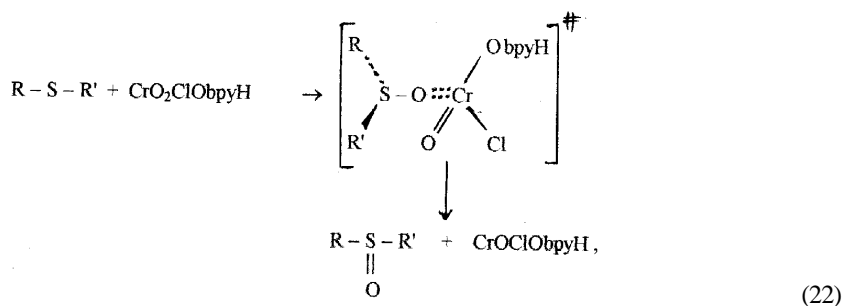
The analysis of the effect of solvents indicates that the transition state is more polar than the reactants. Further, the fact that both cation- and anion-solvating powers of the solvents play important roles suggests that a moderate degree of charge separation takes place during the rate-determining step.

Table 6. Correlation of rate of oxidation of alkyl phenyl sulphides with Pavelich–Taft equation^a.

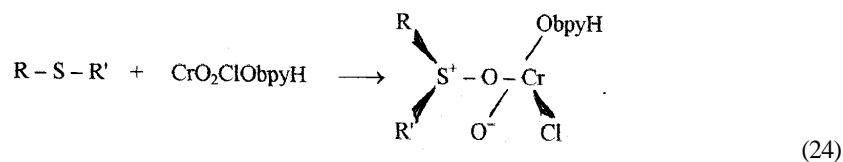
Temp. (K)	r^*	d	R^2	sd
293	-2.45 ± 0.20	0.73 ± 0.02	0.9998	0.001
303	-2.27 ± 0.03	0.66 ± 0.01	0.9999	0.003
313	-2.16 ± 0.01	0.62 ± 0.01	0.9987	0.001
323	-1.93 ± 0.06	0.55 ± 0.02	0.9995	0.005

^aNo. of data points = 5

The experimental results can be accounted for in terms of rate-determining electrophilic oxygen transfer from BPCC to the sulphide as in (22) and (23) below, similar to that suggested for oxidations of sulphides and iodide ions by periodate ion³⁶ and for the oxidation of sulphides by hydrogen peroxide²⁷ and PFC⁶.

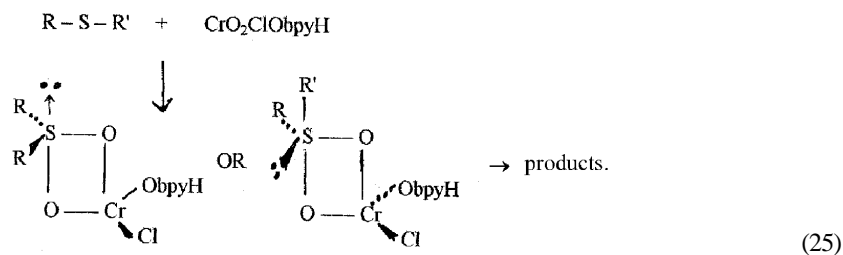


The nucleophilic attack of a sulphide-sulphur on a BPCC-oxygen may be viewed as an $\text{S}_\text{N}2$ process. Low magnitudes of the polar reaction constants are consistent with the development of a polar transition state rather than with the formation of an intermediate with a positive sulphonium centre as depicted in (24) below.



Further, an electrophilic attack on the sulphide-sulphur is confirmed by the positive value of h which indicates that the substituent is better able to stabilize a cationic or electron-deficient site. The low magnitude of h which represents the electronic demand of the reaction, indicates a less-pronounced charge separation in the transition state. This militates against the formation of a sulphonium cation and rather supports a mechanism involving the formation of a polar transition state in the rate-determining step. The formation of a positive sulphonium cation, in the oxidation of sulphides by Cr^{+37} , is more responsive to steric hindrance than observed in the present study. The observed solvent effect also supports an $\text{S}_{\text{N}}2$ -like transition state.

The oxidation of sulphides by BPCC may involve a cyclic intermediate as has been suggested in many reactions of Cr(VI) ³⁸. The cyclic transition state will be highly strained in view of the apical position of a lone pair of electrons or an alkyl group as per



The steric requirements of the (25) will be higher as compared to those of (22) 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 a much larger negative entropy of activation than that observed. The value of the entropy of activation obtained in this reaction is close to the value observed in typical reactions involving oxygen transfer e.g. oxidation of iodide ion by periodate³⁶ and that of MeSPh by hydrogen peroxide²⁷, periodate²⁸ and PFC⁶ ($\Delta S^\ddagger = -96, -115, -113, \text{ and } -89 \text{ J mol}^{-1} \text{ K}^{-1}$ respectively). In the oxidation of vicinal-diols by chromic acid, where formation of a cyclic transition state has been proposed, Chatterjee and Mukherji³⁹ obtained entropies of activation in the range of -174 to $-195 \text{ J mol}^{-1} \text{ K}^{-1}$.

It is of interest to compare here the mode of oxidation of organic sulphide by PFC⁶, PCC⁴⁰, PBC⁷ and BPCC. The oxidation by PFC, PBC and BPCC presented a similar kinetic picture, i.e. the reactions are of first order with respect to the reductants, while in the oxidation by PCC, Michaelis-Menten type kinetics is observed with respect to the reductants. It is possible that the values of the formation constants for the reductant-BPCC complexes are very low. This results in the observation of second-order kinetics. No explanation of the difference is available presently. Kinetic isotope effects, solvent effects (in the oxidation by PCC, the effect of different solvents was not studied) and the dependence of the hydrogen ions are of similar nature in all these reactions, for which essentially similar mechanisms have been proposed. The common mechanism proposed⁸ for the oxidation of diphenyl sulphide by Cr(VI) reagents, in acetic acid, is essentially similar to the one proposed by us.

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