OXIDATION OF ORGANIC SULFIDES BY QUINOLINIUM CHLOROCHROMATE: A KINETIC AND MECHANISTIC APPROACH

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The oxidation of organic sulfides by quinolinium chlorochromate (QCC) resulted the formation of the corresponding organic sulfoxides. These reactions are first order ones with respect to QCC. A Michaelis-Menten type kinetics was observed with respect to the reactants. The reaction is catalyzed by p-toluene sulfonic acid (TsOH). The oxidation was studied in nineteen different organic solvents. An analysis of the solvent effect on 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 done in terms of various single and multiparametric equations. In the reactions of aryl methyl sulfides, the best correlation could be obtained with Charton's LDR and LDRS equations. The oxidation reactions of alkyl phenyl sulfides exhibited an excellent correlation in terms of Pavelich-Taft equation. The negative values of polar reaction constants indicate an electron-deficient sulfur center in the rate- determining step. The proposed reaction mechanism involves the formation of a sulphenium cation intermediate in a slow step

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INTRODUCTION

Various halochromates have been used as mild and selective oxidizing reagents in synthetic organic chemistry.[1] Oxidation of sulfides has been tested with various oxidants.[2] There are several papers published from our laboratory about the kinetic and mechanistic aspects of the oxidation by complex cation containing anionic Cr(VI) species.[1-7] Quinolinium chlorochromate (QCC) is one of the oxidants belong to our interesting field.[2] It is well known that mode of oxidation depends upon the nature of counter-ion attached to the chromium-containing anion. Karunakaran et. al.[8] have reported a mechanism for the oxidation of diphenyl sulfide by various anionic Cr(VI) reagents in acetic acid. In the present article, we report the kinetics of oxidation of thirty-four organic sulfides by QCC in dimethylformamide (DMF) as the solvent. Attempts have been made to correlate rate and structure in these reactions. A probable mechanism of these reactions has been proposed.

EXPERIMENTAL

Materials

The sulfides were either commercial products or prepared by known methods[9] and were purified by distillation under reduced pressure or crystallization. Their purity was checked by comparing their boiling or melting points with the literature values. QCC was prepared by the reported method.[1] p-Toluene-sulfonic acid (TsOH) was used as a proton source. Other solvents were purified by their usual methods.[10]

Product analysis

MeSPh or Me_2S (0.1 mol) and QCC (0.01 mol) was dissolved in the appropriate solvent (50 ml), and the mixture was allowed to stand for 20 h. The solvent was removed in vacuum, the residue was diluted with water and extracted with chloroform (3x50 mL). The organic layer was dried over anhydrous $MgSO_4$, the solvent was removed by evaporation. The IR and 1H NMR spectra of the residue were identical with those of the corresponding sulfoxides. IR bands characteristic of the sulfides and sulfones could not be detected, but strong and broad absorption bands characteristics for sulfoxide[11] appeared at 1050 cm^{-1}. The peak of methyl protons in the NMR spectrum of Me_2S was shifted from 2.1 ppm to 2.6 ppm in the oxidation product. In the corresponding sulfone, the peak should have appeared at 3.0 ppm.[12] Similar experiments were performed with the other sulfides also. In all cases, the products were the corresponding sulfoxides. The oxidation state of chromium in completely reduced reaction mixtures, determined by an iodometric method, was 3.90 ± 0.10.

Kinetic measurements

The reactions were studied under pseudo-first-order conditions by keeping an excess (×15 or greater) of the sulfide over QCC. 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 QCC 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 [QCC] against time. Duplicate kinetic runs unambiguously showed that the rate constants are reproducible to within ±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 calculated from the known relation $k_2 = k_{obs}/$ [sulfide]. Simple and multivariate regression analyses were also carried out by the least -squares method.

RESULTS AND DISCUSSION

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

$$R–S–R' + O_2CrClOQH \longrightarrow R–SO–R' + OCrClOQH \quad (1)$$
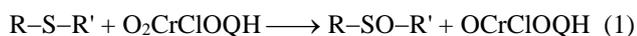
QCC undergoes two-electron redox transformation. This result is in accordance with the earlier observations about structurally similar other halochromates also. It has already been shown that both PFC[13] and PCC[14] reacted as two electron oxidants and are reduced to chromium (IV) species. The oxidation state of chromium was determined by magnetic susceptibility, ESR and IR studies.

Rate law

The reactions are of first order with respect to QCC. Figure 1 depicts a typical kinetic run. The pseudo-first order rate constant, k_{obs} was found to be independent of the initial concentration of QCC. The reaction rate increases with increase in the concentration of the sulfide but not linearly (Table 1). A plot of $1/k_{obs}$ against $1/[\text{sulfide}]$ is linear ($r > 0.995$) with an intercept on the rate-ordinate (Figure 2). Thus, Michaelis-Menten type kinetics are observed with respect to the sulfide. This leads to the postulation of following overall mechanism (2) and (3) and rate law (4).

$$\text{Sulfide} + \text{QCC} \underset{}{\overset{K}{\rightleftharpoons}} [\text{Intermediate}] \quad (2)$$

$$[\text{Intermediate}] \overset{k_2}{\longrightarrow} \text{Products} \quad (3)$$
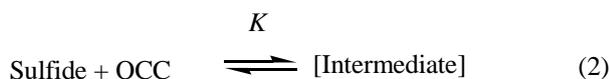
$$\text{Rate} = Kk_2[\text{sulfide}][\text{QCC}]/(1 + K[\text{sulfide}]) \quad (4)$$

The dependence of reaction rate on the reductant concentration was studied at various temperatures, and the values of K and k_2 were evaluated as usual from the double reciprocal plots. The thermodynamic parameters of the complex formation and activation parameters of the decomposition of the complexes were calculated from the individual values of K and k_2 respectively at different temperatures (Tables 2 and 3). Figure 2 depict a typical kinetic run.

Test reaction for free radicals

The oxidation of methyl phenyl sulfide, in an inert atmosphere (N$_2$), failed to induce the polymerization reaction of acrylonitrile. The addition of acrylonitrile had no any effect on the rate of oxidation (Table 1). To confirm the absence/role 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 proved to be unchanged and could be recovered almost quantitatively.

Table 1. Rate constants for the oxidation of MeSPh by QCC at 298 K

10^3 [QCC] mol dm^{-3}	[Sulfide] mol dm^{-3}	[TsOH], mol dm^{-3}	$10^4 k_{obs}$, s^{-1}
1.0	0.10	0.0	11.0
1.0	0.20	0.0	16.2
1.0	0.40	0.0	21.2
1.0	0.60	0.0	23.6
1.0	0.80	0.0	25.1
1.0	1.00	0.0	26.0
1.0	1.50	0.0	27.4
1.0	3.00	0.0	28.9
2.0	0.40	0.0	15.3
4.0	0.40	0.0	17.1
6.0	0.40	0.0	16.8
8.0	0.40	0.0	15.0
1.0	0.20	0.0	22.5
^{a}contained 0.001 M acrylonitrile			
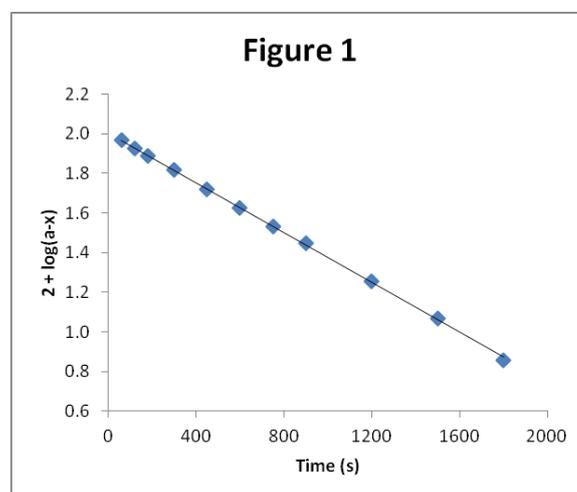
Figure 1. Oxidation of methyl phenyl sulfide by QCC: A typical kinetic run.
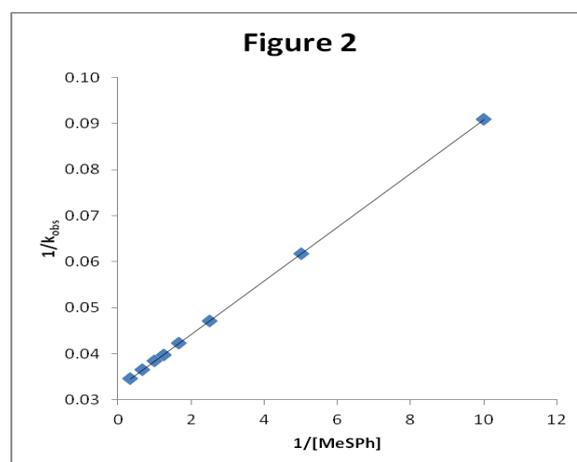
Figure 2. A double reciprocal plot: $1/k_{obs}$ versus $1/$[Sulfide]

Table 2. Formation constants of QCC−sulfide complexes and thermodynamic parameters

Substituent	K, dm³ mol⁻¹				$-\Delta H^*$ kJ mol⁻¹	$-\Delta S^*$ J mol⁻¹ K⁻¹	$-\Delta G^*$ kJ mol⁻¹
	288 K	298 K	308 K	318 K			
H	6.39	5.65	4.92	4.25	12.8±0.3	21±1	6.76±0.7
p-Me	5.22	4.51	3.80	3.07	15.9±0.7	33±2	6.18±0.5
p-OMe	6.16	5.43	4.70	4.05	13.1±0.3	22±1	6.66±0.5
p-F	5.94	5.24	4.51	3.78	13.9±0.6	25±2	6.56±0.6
p-Cl	5.85	5.15	4.43	3.70	14.1±0.6	26±2	6.51±0.6
p-NO₂	5.99	5.28	4.57	3.84	13.7±0.5	24±2	6.58±0.6
p-COMe	6.03	5.33	4.60	3.90	13.5±0.5	24±2	6.60±0.6
p-COOMe	6.21	5.51	4.78	4.03	13.4±0.6	23±2	6.68±0.6
p-Br	5.76	5.05	4.35	3.62	14.2±0.6	26±2	6.47±0.5
p-NHAc	5.31	4.60	3.85	3.17	15.6±0.6	32±2	6.22±0.6
p-NH₂	5.49	4.78	4.03	3.35	15.0±0.5	30±2	6.32±0.7
m-Me	5.36	4.65	3.95	3.24	15.2±0.6	30±2	6.26±0.5
m-OMe	5.75	5.04	4.30	3.58	14.5±0.6	27±2	6.46±0.5
m-Cl	5.90	5.18	4.48	3.75	13.9±0.5	25±2	6.54±0.6
m-Br	6.12	5.42	4.70	3.97	13.4±0.5	23±2	6.64±0.6
m-I	5.58	4.87	4.15	3.44	14.7±0.6	29±2	6.37±0.5
m-NO₂	6.30	5.59	4.84	4.16	13.0±0.4	22±1	6.72±0.6
m-CO₂Me	5.67	4.93	4.25	3.54	14.3±0.5	27±2	6.42±0.5
o-Me	6.05	5.35	4.62	3.87	13.8±0.6	25±2	6.61±0.5
o-OMe	5.82	5.13	4.36	3.69	14.1±0.5	26±2	6.50±0.4
o-NO₂	6.13	5.40	4.68	3.96	13.5±0.5	24±1	6.64±0.4
o-COOMe	5.90	5.17	4.44	3.76	13.9±0.4	25±1	6.53±0.3
o-Cl	6.22	5.52	4.77	4.05	13.4±0.5	23±2	6.69±0.4
o-Br	5.88	5.18	4.45	3.75	13.9±0.5	25±2	6.53±0.4
o-I	5.77	5.04	4.35	3.60	14.4±0.6	27±2	6.47±0.5
o-NH₂	6.02	5.32	4.57	3.87	13.6±0.5	24±2	6.59±0.4
Alkyl phenyl sulfides							
Et	6.39	5.70	4.92	4.25	12.9±0.4	21±1	6.76±0.3
Pr	5.85	5.15	4.43	3.70	14.1±0.6	26±2	6.51±0.5
i-Pr	6.48	5.78	5.05	4.35	12.6±0.4	20±1	6.81±0.3
t-Bu	5.67	4.93	4.25	3.49	14.7±0.6	28±2	6.42±0.5
Other sulfides							
Me₂S	5.94	5.25	4.53	3.76	14.0±0.7	26±2	6.56±0.5
Pr₂S	6.21	5.51	4.76	4.07	13.2±0.4	22±1	6.68±0.3
Ph₂S	5.85	5.11	4.43	3.71	13.9±0.5	25±2	6.51±0.4

Table 3. Rate constants and activation parameters of the decomposition of QCC-sulfide complex.

Substituent	$10^4 \, k_2$ dm³ mol⁻¹ 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	14.4	30.6	62.1	123	51.8±0.1	120±1	87.3±0.2
p-Me	32.4	65.7	126	246	48.7±0.5	124±1	85.5±0.4
p-OMe	75.6	153	288	522	46.4±0.2	125±1	83.4±0.2
p-F	14.4	31.5	65.7	135	54.2±0.3	112±1	87.3±0.2
p-Cl	9.36	20.7	43.5	89.1	54.6±0.1	114±1	88.3±0.1
p-NO₂	0.72	1.80	4.23	9.90	63.8±0.4	103±1	94.4±0.3
p-COMe	1.89	4.50	10.1	22.0	59.7±0.3	109±1	92.1±0.2
p-COOMe	2.82	6.57	14.4	31.5	58.6±0.4	110±1	91.2±0.3
p-Br	9.21	20.3	42.8	88.2	54.7±0.2	113±1	88.4±0.2
p-NHAc	36.0	74.7	144	279	49.2±0.3	121±1	85.2±0.2
p-NH₂	288	540	963	1660	41.9±0.1	129±1	80.3±0.1
m-Me	27.0	55.8	108	207	49.0±0.2	124±2	85.9±0.4
m-OMe	33.3	67.5	126	234	46.8±0.2	130±1	85.4±0.2

m-Cl	5.19	11.7	24.3	49.5	54.6±0.2	119±1	89.8±0.2
m-Br	5.12	11.3	23.8	48.9	54.7±0.2	118±1	89.8±0.2
m-I	6.18	13.5	28.3	57.6	54.1±0.2	119±1	89.4±0.2
m-NO$_2$	0.53	1.35	3.17	7.38	64.1±0.3	104±1	95.1±0.3
m-CO$_2$Me	2.52	5.94	13.5	28.3	59.0±0.2	109±1	91.4±0.2
o-Me	6.12	13.5	30.3	63.9	57.2±0.5	108±2	89.3±0.4
o-OMe	16.2	36.0	73.5	144	52.8±0.3	115±1	87.0±0.2
o-NO$_2$	0.32	0.86	2.20	5.49	69.5±0.4	90±1	96.2±0.3
o-COOMe	0.75	1.92	4.71	11.3	66.2±0.4	94±1	94.2±0.4
o-Cl	1.62	4.05	9.54	22.1	63.7±0.3	97±1	92.4±0.2
o-Br	1.21	3.06	7.36	17.1	64.6±0.3	96±1	93.0±0.2
o-I	0.92	2.37	5.83	14.0	66.5±0.4	92±1	93.7±0.3
o-NH$_2$	54.0	109	207	387	47.3±0.1	124±1	84.2±0.2
Alkyl phenyl sulfides							
Et	23.4	50.4	99.0	198	70.3±0.2	59±1	87.8±0.2
Pr	14.3	31.5	68.4	142	74.7±0.2	48±1	88.8±0.2
i-Pr	18.0	41.4	89.1	180	75.4±0.4	43±1	88.1±0.3
t-Bu	4.07	11.2	29.7	75.2	81.4±0.8	33±3	91.1±0.6
Other sulfides							
Me$_2$S	31.5	59.4	117	207	67.0±0.9	69±3	87.4±0.8
Pr$_2$S	54.0	99.0	180	342	65.3±0.9	71±3	86.4±0.7
Ph$_2$S	7.02	15.3	31.5	67.5	76.8±0.9	49±3	91.2±0.7

Effect of acidity

The reaction is catalysed by TsOH (Table 4). The TsOH-dependence has the form $k_{obs} = a + b$ [TsOH]. The values of a and b for methyl phenyl sulfide are $10.4±0.57±10^{-4}$ s^{-1} and $18.8±0.95±10^{-4}$ mol^{-1}dm^3 s^{-1} respectively ($r^2 = 0.9980$). Therefore, the experimental rate law can be given in the following form:

$$\text{Rate} = k_2 \text{ [QCC] [sulfide]} + k_3 \text{ [QCC] [sulfide] [TsOH]} \quad (5)$$

Table 4. Dependence of the reaction rate on hydrogen–ion concentration

[H+] mol dm^{-3}	0.10	0.20	0.40	0.60	0.80	1.00
$10^4 k_{obs}$ s^{-1}	12.3	14.4	16.4	21.0	25.2	29.3

[sulfide] 0.10 mol dm^{-3}, [QCC] 0.001 mol dm^{-3}, T 298 K

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 QCC and its reaction with primary and secondary alcohols. There was no reaction with the solvents chosen. The kinetics were similar in all the solvents. The values of k_2 and K are recorded in Table 5.

There is a linear correlation between the activation enthalpies and entropies of the oxidation of the thirty-four sulfides (r = 0.9693), indicating the operation of a compensation effect.[15] The value of the isokinetic temperature is 607±31 K. However, according to Exner[16] an isokinetic relationship between the calculated values of enthalpies and entropies is often vitiated by the random experimental errors associated with them. Exner suggested an alternative method for establishing the isokinetic relationship. An Exner's plot between log k_2 at 288 K and at 318 K was linear ($r^2 = 0.9962$, slope = 0.8302 ± 0.0090). The value of isokinetic temperature evaluated as usual from the Exner's plot is 656±65 K. The linear isokinetic correlation implies that all the sulfides studied 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.

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 (6) of Kamlet et al.[17]

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha \quad (6)$$

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 that out of the 18 solvents, 13 have a value of zero for α. The results of correlation analysis in terms of equation (6), a biparametric equation involving π^* and β, and separately with π^* and β are given below in eqns. (7-10). We have used the standard deviation (*sd*), the coefficient of multiple determination (R^2), and Exner's[18] parameter, ψ, as the measures of goodness of fit. Here *n* is the number of data points.

Table 5. Solvent effect on the oxidation of Me-S-Ph by QCC at 318 K

Solvents	K dm^{-3} mol^{-1}	$10^4 k_{obs}$ s^{-1}	Solvents	K dm^{-3} mol^{-1}	$10^4 k_{obs}$ s^{-1}
Chloroform	4.55	85.1	Toluene	5.13	16.2
1,2-Dichloroethane	4.83	70.8	Acetophenone	5.00	81.3
Dichloromethane	4.41	77.6	THF	4.57	30.2
DMSO	5.49	269	t-Butyl alcohol	4.33	35.5
Acetone	4.76	57.5	1,4-Dioxane	4.71	26.9
DMF	4.25	123	1,2-Dimethoxyethane	5.04	17.0
Butanone	5.13	41.7	Carbon disulphide	4.22	6.46
Nitrobenzene	5.04	93.3	Acetic Acid	5.15	33.9
Benzene	4.95	17.8	Ethyl Acetate	5.23	22.4
Cyclohexane	4.62	1.51			

$$\log k_2 = -4.26 + 1.88(\pm 0.19)\,\pi^* + 0.16(\pm 0.16)\,\beta + 0.3(\pm 0.15)\,\alpha \quad (7)$$
$$R^2 = 0.8869;\ sd = 0.18;\ n = 18;\ \psi = 0.37$$

$$\log k_2 = -4.34 + 1.77(\pm 0.20)\,\pi^* + 0.27(\pm 0.17)\,\beta \quad (8)$$
$$R^2 = 0.8528;\ sd = 0.20;\ n = 18;\ \psi = 0.41$$

$$\log k_2 = -4.39 + 1.84\ (\pm 0.21)\,\pi^* \quad (9)$$
$$r^2 = 0.8273;\ sd = 0.21;\ n = 18;\ \psi = 0.39$$

$$\log k_2 = -2.63 + 0.59(\pm 0.39)\,\beta \quad (10)$$
$$r^2 = 0.1255;\ sd = 0.47;\ n = 18;\ \psi = 0.96$$

Kamlet's[17] 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. eqn. 7). The major contribution is of solvent polarity. It alone accounted for *ca.* 83 % of the data. Both β and α play relatively minor roles.

The data on the solvent effect obtained were analyzed in terms of Swain's equation[19] of cation- and anion-solvating concept of the solvents as well.

$$\log k_2 = aA + bB + C \quad (11)$$

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 analyzed in terms of Eqn. (11), separately with *A* and *B* and with (*A* + *B*).

$$\log k_2 = 1.38(\pm 0.04)\,A + 1.76(\pm 0.03)\,B - 3.97 \quad (12)$$
$$R^2 = 0.9965;\ sd = 0.03;\ n = 19;\ \psi = 0.06$$

$$\log k_2 = 1.13(\pm 0.58)\,A - 2.76 \quad (13)$$
$$r^2 = 0.1827;\ sd = 0.47;\ n = 19;\ \psi = 0.93$$

$$\log k_2 = 1.65(\pm 0.24)\,B - 3.52 \quad (14)$$
$$r^2 = 0.7271;\ sd = 0.27;\ n = 19;\ \psi = 0.54$$

$$\log k_2 = 1.63 \pm 0.05\ (A + B) - 3.96 \quad (15)$$
$$r^2 = 0.9820;\ sd = 0.07;\ n = 19;\ \psi = 0.14$$

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 permittivities of the solvents. However, a plot of log k_2 against the inverse of the relative permittivity is not linear ($r^2 = 0.5044$; $sd = 0.36$; $\psi = 0.72$).

Correlation analysis of reactivity

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

Aryl methyl sulfides

The correlation of the effect of substituents on the reactivity has been widely attempted in terms of the Hammett equation[20] or with dual substituent-parameter equations.[21,22] In the late 1980s, Charton[23] 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 most important 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 using the LDR equation. In our present work, we have applied the LDR equation (16) to the rate constants, k_2.

$$\log k_2 = L\,\sigma_l + D\,\sigma_d + R\,\sigma_e + h \quad (16)$$

Here, σ_l is a localized (field and/or inductive) effect parameter, and 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 (17).

Table 6. Temperature dependence of the reaction constants for the oxidation of organic sulfides by QCC

T/K	− L	− D	− R	− S	η	R²	sd	ψ	P_D	P_S
Para-substituted										
288	1.62	1.98	1.79	-	0.90	0.9999	0.008	0.01	36.7	-
298	1.53	1.89	1.69	-	0.89	0.9998	0.006	0.02	37.0	-
308	1.43	1.80	1.60	-	0.89	0.9999	0.004	0.01	37.3	-
318	1.35	1.71	1.48	-	0.87	0.9989	0.005	0.04	37.7	-
Meta-substituted										
288	1.88	1.53	1.36	-	0.89	0.9998	0.002	0.02	32.1	-
298	1.79	1.44	1.32	-	0.92	0.9998	0.004	0.02	31.6	-
308	1.71	1.34	1.26	-	0.94	0.9999	0.006	0.01	31.1	-
318	1.62	1.26	1.15	-	0.91	0.9999	0.001	0.01	31.3	-
Ortho-substituted										
288	1.53	1.61	1.37	1.25	0.85	0.9999	0.005	0.01	35.7	21.7
298	1.42	1.53	1.27	1.18	0.83	0.9998	0.004	0.01	36.2	21.8
308	1.35	1.44	1.17	1.08	0.81	0.9999	0.001	0.01	36.4	21.4
318	1.26	1.34	1.11	0.99	0.83	0.9999	0.004	0.02	36.1	21.1

$$\sigma_D = \eta\sigma_e + \sigma_d \qquad (17)$$

Here η represents the electronic demand of the reaction site and represents the ratio of the 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 Charton[23] therefore, modified the LDR equation to generate the LDRS equation (18).

$$\log k_2 = L\sigma_l + D\sigma_d + R\sigma_e + S\upsilon + h \qquad (18)$$

where υ is the known Charton's steric parameter based on Van der Waals radii[24].

The rates of oxidation of ortho-, meta-, and para-substituted sulfides show excellent correlations in terms of the LDR/LDRS equations (Table 6). The values of the independent variables, σ_l, σ_d, σ_e and υ, were obtained from the work of Charton and Charton.[19] Though the number of data points is less than the optimum number, the correlations are excellent as per Exner's[16] 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 (18), reflecting 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_l, σ_d and σ_e, (ii) σ_d, σ_e and υ, and (iii) σ_l, σ_e and υ. The absence of significant correlations [eqns. (19-21)] showed that all the four substituent constants are significant.

$$\log k_2 = -1.99(\pm 0.48)\sigma_l - 1.33(\pm 0.39)\sigma_d$$
$$-1.99(\pm 2.76)\sigma_e - 2.87 \qquad (19)$$
$$R^2 = 0.8926; \ sd = 0.29; \ n = 10; \ \psi = 0.40$$

$$\log k_2 = -1.89(\pm 0.44)\sigma_d + 0.51(\pm 3.51)\sigma_e - 1.84(\pm 0.54)$$
$$\upsilon - 2.64 \qquad (20)$$
$$R^2 = 0.8528; \ sd = 0.34; \ n = 10; \ \psi = 0.47$$

$$\log k_2 = -2.12(\pm 0.88)\sigma_l - 5.39(\pm 4.41)\sigma_e - 0.71(\pm 0.88)$$
$$\upsilon - 2.42 \qquad (21)$$
$$R^2 = 0.6823; \ sd = 0.50; \ n = 10; \ \psi = 0.69$$

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[24] of the delocalized effect, P_D is given by the following equation (22).

$$P_D = (|D| \times 100)/(|L| + |D| + |R|) \qquad (22)$$

Similarly, the percent contribution of the steric parameter[24] to the total effect of the substituent, P_S, was determined by using equation (23).

$$P_S = (|S| \times 100)/(|L| + |D| + |R| + |S|) \qquad (23)$$

The values of P_D and P_S are also recorded in Table 6. The value of P_D for the oxidation of para-substituted sulfides is *ca.* 52 % whereas the corresponding values for the meta- and ortho-sobstituted aldehydes are *ca.* 39 and 49 % 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.

In earlier studies on the oxidations of organic 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),[25] periodate (-1.40),[26] permanganate (-1.52),[27] and peroxydisulfate (-0.56).[28] Large negative reaction constants were exhibited by oxidations involving the formation of halogeno-sulfonium cations e.g. by chloramine-T(-4.25),[29] bromine (-3.2)[30] and N-bromoacetamide (-3.75).[31] In the oxidation by N-chloroacetamide (NCA)[32] the values of the field (ρ_I) and resonance (ρ^+_R), at 298 K are -1.3 and -1.7 respectively.

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 analyzed in terms of Pavelich--Taft's[33] dual substituent-parameter (DSP) equation (24).

$$\log k_2 = \rho^* \sigma^* + \delta E_s + \log k_0 \qquad (24)$$

The correlations are excellent (Table 7). 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 7. Correlation of rate of oxidation of alkyl phenyl sulfides with Pavelich-Taft equation

T, K	$-\rho^*$	δ	R^2	sd	ψ
288	2.79±0.04	0.88±0.01	0.9999	0.003	0.01
298	2.71±0.06	0.81±0.01	0.9998	0.006	0.02
308	2.56±0.04	0.71±0.01	0.9998	0.004	0.02
318	2.39±0.09	0.61±0.02	0.9989	0.007	0.04

[a] No. of data points = 5

Mechanism

The observed dependence on TsOH suggests that the reaction follows two mechanistic pathways, one TsOH-catalysed and the other uncatalysed. The catalytic effect of TsOH can be attributed to a protonation of QCC to give a stronger oxidant and electrophile (25).

$$O_2CrClOQH + TsOH \rightleftarrows [OCr(OH)ClOQH]^+[TsO]^- \qquad (25)$$

In view of the absence of any effect of the 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 an intermediate in a rapid pre-equilibrium. With present set of data, it is difficult to state the definite nature of the intermediate complex. The most logical mode of interaction between sulfides and QCC would, therefore, be the 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 initially 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 QCC 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. The steric requirements of the reaction will be higher as compared to those of reaction, 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.
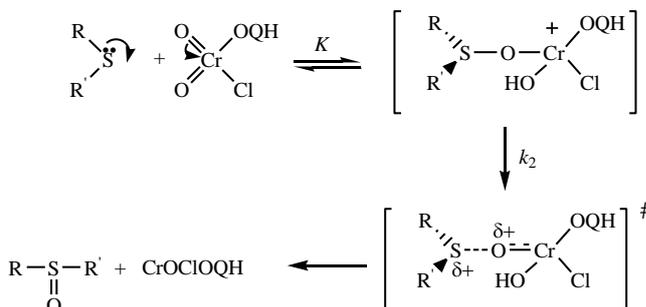
Scheme 1. Mechanism of the oxidation of sulfides by QCC.

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