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A Mechanistic and Correlative Study on Sulfide Oxidation by Diethylammonium Chlorochromate

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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Original Research Article

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Abstract

The process of turning organic sulfides into their sulfoxides using diethylammonium chlorochromate (DEACC) occurred at first order concerning DEACC. On the other hand, the reaction shows Michaelis–Menten-type kinetics when it comes to the sulfide substrate. We used both single-parameter and multi-parameter correlation equations to conduct a kinetic study of thirty-four distinct sulfides. Charton's LDR and LDRS equations gave the most accurate correlations for aryl methyl sulphides. The polar regression coefficients were negative in these cases. The rate data for alkyl phenyl sulfides matched up quite well with the Pavelich–Taft equation. Also, the oxidation of methyl phenyl sulfide was studied in nineteen distinct organic solvents. Kamlet–Taft and Swain's multiparametric models were used to look at how the polarity and other properties of the solvent affected the reaction. Based on the kinetic measurements, it has been suggested that a reaction mechanism includes the creation of a sulfurane intermediate during the phase that controls the rate.

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1. Introduction

Halochromates have historically served as mild and selective oxidising agents in synthetic organic chemistry (Corey & Suggs, 1975; Guziec & Luzzio, 1980; Bhattacharjee et al. 1982; Dayal et al., 1972). Diethylammonium chlorochromate (DEACC) is a well-established oxidising agent, primarily employed for the oxidation of primary aliphatic alcohols (Singh et al., 2009) and for the oxidative regeneration of carbonyl compounds from oximes (Choudhary et al., 2024). Despite its broad applications, the kinetics of organic sulphide oxidation by DEACC have not yet been explored. In the present study, we investigate the kinetic and mechanistic aspects of oxidation reactions mediated by complexed Cr(VI) species, building upon extensive previous research (Yajurvedi et al., 2023; Choudhary et al., 2024; Vadera et al., 2010; Karunakaran, 1999), which identified a common mechanistic pathway for the oxidation of diphenyl sulphide by various Cr(VI) reagents in acetic acid (Karunakaran, 1999). Here, we report the kinetics of oxidation of thirty-four organic sulphides by DEACC in dimethylformamide (DMF) as the solvent. Additionally, the study considers the influence of the solvent environment on the oxidation kinetics of aldehydic compounds by DEACC, highlighting the critical role of solvent effects in modulating reaction rates (Chandora, 2021).

This work has two purposes. Initially, to ascertain if DEACC exhibits distinct behaviour compared to other Cr (VI) reagents, and subsequently to investigate the influence of structure and solvent on the reaction rate. Efforts have also been undertaken to link the rate and structure of this reaction. A potential mechanism has been suggested. Kinetic studies of sulfides are essential for understanding the rates, mechanisms, and influencing factors (such as pH, temperature, and concentration) of sulfide-related reactions. These studies are critical for industrial, environmental, and geochemical applications, particularly in predicting mineral formation, optimizing ore leaching, improving battery technology, and managing corrosion

2. Experimental

2.1 Materials*:*

The sulphides were either commercially accessible or synthesized using accepted procedures (Zincke & Müller, 1913), and were refined either by distillation under lower pressure or recrystallisation. Their purity was assessed by comparing their boiling or melting points with the values in the literature. DEACC was synthesized using the technique described by Singh et al. 2009). Toluene p-sulfonic acid (TsOH) served as a source of hydrogen ions.

2.2 Product Analysis

After dissolving MeSPh or Me_2S (0.1 mol) and DEACC (0.01 mol) in 50 ml of DMF, the mixture was left to stand for about 20 hours. Under lower pressure, the majority of the solvent was evaporated. The chloroform (3×50 ml) was used to remove the residue after diluting it with water. After drying the chloroform layer on top of anhydrous magnesium sulphate, the solvent was evaporated off, and the remaining material was studied using infrared and ^1H nuclear magnetic resonance spectroscopy. Comparing the spectra to the equivalent sulfoxides revealed no differences. There were no sulphide or sulfone peaks that could be identified. An extensive and robust absorption at 1050 cm^{-1} was observed in the product's infrared spectra. There was no presence of a band at 1330 or 1135 cm^{-1}, which are indicative of sulfones (Pouchert, 1985). In the instance of Me_2S, the peak attributed to methyl protons in NMR spectroscopy moved from 2.1 τ, in the sulphide to 2.6 τ in the final product. According to Pouchert (1980), the peak should have been seen at 3.0 τ in the related sulfone (Pouchert, 1980). All of the sulphides were subjected to the same experimental protocols. The sulfoxides were the end products in every instance. According to an iodometric approach, the chromium oxidation state in fully reduced reaction mixtures was +4.

2.3 Kinetic Measurements

The oxidation reactions were conducted under pseudo-first-order conditions by maintaining a large excess (≥15-fold) of the sulfide relative to diethylammonium chlorochromate (DEACC). The concentration of DEACC was

typically fixed at 0.001 mol dm^{-3}, while the concentration of the sulfide varied depending on its reactivity. For highly reactive sulfides such as p-amino-, o-amino-, and p-methoxy-phenyl methyl sulfides, sulfide concentrations ranged from 0.01 to 0.1 mol dm^{-3} at 298 K. At other temperatures, a standard concentration of 0.05 mol dm^{-3} was employed. In contrast, for less reactive sulfides, including nitro- and halo-substituted phenyl methyl sulfides, higher concentrations between 2 and 5 mol dm^{-3} were used, adjusted based on temperature and solvent requirements. Unless stated otherwise, N, N-dimethylformamide (DMF) served as the reaction medium. All reactions were performed at constant temperature (±0.1 K). The progress of the reaction was monitored spectrophotometrically by following the decrease in DEACC absorbance at 380 nm, up to approximately 80% completion. Pseudo-first-order rate constants (k_{obs}) were determined from the linear plots of log [DEACC] versus time, with correlation coefficients typically exceeding 0.995. Duplicate kinetic runs confirmed the reproducibility of the rate constants within ±3%. Both simple and multiple regression analyses were conducted using the least squares method.

3. Results and Discussion

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

$$R{-}S{-}R' \; + \; O_2CrClO^- \, N^+H_2Et_2 \rightarrow \; R - \underset{\underset{O}{||}}{S} - R' \; + \; OCrClO^-N^+H_2Et_2 \qquad (1)$$

DEACC undergoes a two-electron change. This is according to the earlier observations with structurally similar other halochromates reported (Yajurvedi et al. 2023; Choudhary et al. 2024; Vadera et al. 2010). It has already been shown that both PFC (Brownet al. 1979) and PCC (Bhattacharjee et al. 1987) act as two electron oxidants and are reduced to chromium (IV) species by determining the oxidation state of chromium by magnetic susceptibility, Electron Spin Resonance (ESR) and Infra-red (IR) studies.

3.1 Rate Laws

The reactions were determined to be first order with respect to DEACC, as evidenced by linear plots of log[DEACC] versus time in individual kinetic runs ($r^2 > 0.995$). Moreover, the observed rate constant, kobsk_{\text{obs}}kobs, was found to be independent of the initial DEACC concentration. The reaction order with respect to the sulfide substrate was determined to be less than unity (Table 1).

A plot of 1/kobs1/k_{\text{obs}}1/kobs versus 1/[sulfide]1/[{\rm sulfide}]1/[sulfide] produced a straight line with a finite intercept on the rate ordinate (Fig. 1), indicating that the reaction follows Michaelis–Menten-type kinetics with respect to the sulfide substrate. Based on these observations, an overall reaction mechanism was proposed, and the corresponding rate law is expressed as Equation (4).

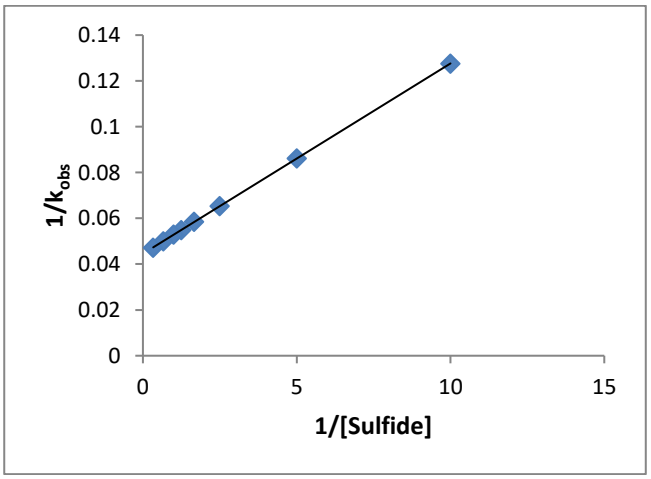


Fig. 1. Oxidation of MeSPh by DEACC: A double reciprocal plot

Table 1. Oxidation rate constants of methyl phenyl sulfide by DEACC at 298 K

10^3 [DEACC] (mol dm^{-3})	[MeSPh] (mol dm^{-3})	[TsOH] (mol dm^{-3})	$10^4 k_{obs}$ (mol dm^{-3})
1.0	0.10	0.00	7.84
1.0	0.20	0.00	11.6
1.0	0.40	0.00	15.3
1.0	0.60	0.00	17.1
1.0	0.80	0.00	18.2
1.0	1.00	0.00	18.9
1.0	1.50	0.00	20.0
1.0	3.00	0.00	21.2
2.0	0.40	0.00	14.5
4.0	0.40	0.00	15.8
6.0	0.40	0.00	15.0
8.0	0.40	0.00	16.2
1.0	0.20	0.00	12.6*

[a] *contained 0.001 M acrylonitrile*

$$\text{Sulfide} + \text{DEACC} \overset{K}{\leftrightarrows} [\text{complex}] \quad (2)$$

$$[\text{Complex}] \xrightarrow{k_2} \text{Products} \quad (3)$$

$$\text{Rate} = k_2 K [\text{Sulfide}] [\text{DEACC}] / (1 + K [\text{Sulfide}]) \quad (4)$$

At various temperatures, the relationship between k_{obs} and sulphide content was examined, and the double reciprocal plots were used to calculate K and k_2. The values of K and k_2 at various temperatures were used to compute the thermodynamic parameters for the complex formation and activation parameters of the complexes' disproportionation at 298 K (Tables 2 and 3). A typical kinetic run is shown in Fig. 2.

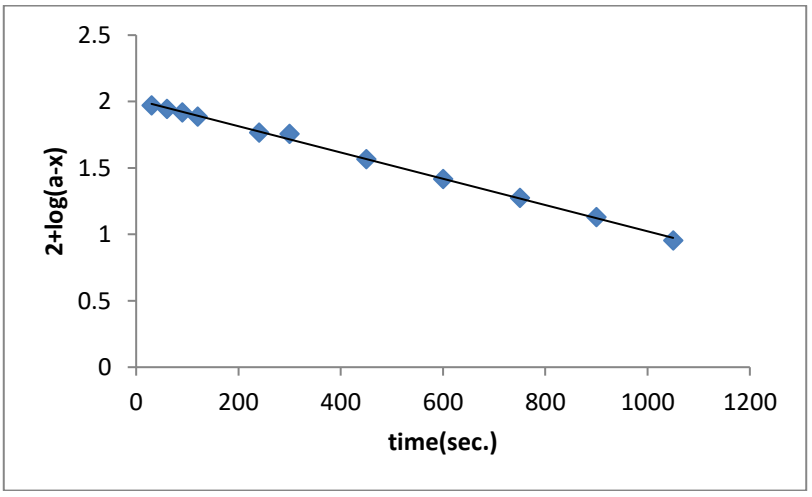


Fig. 2. Oxidation of MeSPh by DEACC: A Typical Kinetic Run

Table 2. Mechanistic study of DEACC–sulfide complex decomposition: rate constants and activation energy

$10^4 k_2$ / (dm^3 $mol^{-1}s^{-1}$)					ΔH^*	$-\Delta S^*$	ΔG^*
Substituent	**288 K**	**298 K**	**308 K**	**318 K**	**(kJ mol^{-1})**	**(J $mol^{-1}K^{-1}$)**	**(kJ mol^{-1})**
H	8.28	22.5	56.7	144	69.7±0.6	62±2	88.1±0.4
p-Me	16.2	44.1	106	261	67.6±0.5	64±2	86.5±0.4

10^4k_2 / (dm^3 $mol^{-1}s^{-1}$)					ΔH^*	$-\Delta S^*$	ΔG^*
Substituent	**288 K**	**298 K**	**308 K**	**318 K**	**(kJ mol^{-1})**	**(J $mol^{-1}K^{-1}$)**	**(kJ mol^{-1})**
p-Ome	36.0	92.7	216	522	65.0±0.6	66±2	84.6±0.5
p-Cl	5.76	16.2	42.5	111	72.4±0.5	56±1	88.9±0.4
p-Br	5.64	15.3	41.7	108	72.5±0.7	56±1	89.0±0.5
p-F	8.82	24.3	63.0	162	71.2±0.5	57±1	87.9±0.4
p-NO_2	0.54	1.71	5.12	14.4	80.8±0.3	46±1	94.5±0.2
p-COOMe	1.80	5.40	14.4	39.6	75.5±0.6	55±2	91.7±0.5
p-NH_2	117	279	621	1350	59.4±0.2	76±1	81.9±0.1
p-COMe	1.26	3.87	10.8	30.6	78.1±0.6	49±2	92.5±0.5
p-NHAc	18.0	48.6	117	288	67.5±0.5	63±1	82.6±0.4
m-Me	15.3	39.6	95.4	234	66.4±0.6	69±2	86.7±0.5
m-Ome	18.0	45.9	108	252	64.3±0.3	75±1	86.4±0.2
m-Cl	3.15	8.73	22.8	60.3	72.2±0.7	62±2	90.4±0.6
m-Br	3.06	8.63	22.5	59.5	72.5±0.5	61±2	90.5±0.4
m-I	3.69	10.8	27.0	69.3	71.4±0.6	63±2	90.0±0.5
m-NO_2	0.36	1.17	3.42	9.99	81.5±0.4	47±1	95.5±0.3
m-CO_2Me	1.62	4.77	12.6	34.2	74.5±0.6	59±2	92.0±0.5
o-Me	3.90	11.7	30.6	83.7	74.8±0.7	51±2	89.8±0.6
o-OMe	9.99	28.8	72.0	180	70.5±0.5	58±1	87.6±0.4
o-NO_2	0.19	0.68	2.16	6.93	88.4±0.4	29±2	96.8±0.5
o-COOMe	0.47	1.53	4.77	14.4	84.3±0.6	36±2	94.7±0.5
o-Cl	1.05	3.33	9.81	28.8	81.3±0.6	39±2	92.8±0.5
o-Br	0.79	2.61	7.65	22.7	82.3±0.5	38±1	93.5±0.4
o-I	0.62	2.07	6.30	18.0	82.9±0.2	38±1	94.0±0.1
o-NH_2	33.3	85.5	198	477	84.6±0.6	68±2	84.8±0.5
Alkyl phenyl sulfides							
Et	12.6	36.0	91.8	225	70.5±0.3	56±1	87.0±0.2
Pr	8.10	23.4	62.1	162	73.3±0.3	50±1	88.0±0.2
i-Pr	9.90	30.6	81.0	216	75.3±0.6	41±2	87.4±0.4
t-Bu	2.25	8.19	25.2	75.6	86.3±0.6	15±2	90.7±0.4
Other Sulfides							
Me_2S	26.1	65.7	171	414	69.7±0.7	59±2	85.4±0.6
Pr_2S	41.4	99.0	243	535	64.7±0.9	66±3	84.4±0.8
Ph_2S	4.95	11.4	42.3	117	77.9±0.7	38±2	89.1±0.6

Table 3. Formation constants of DEACC−Sulfides complexes and their thermodynamic parameters

K/ (dm^3 mol^{-1})					$-\Delta H^*$	$-\Delta S^*$	$-\Delta G^*$
Substituent	**288 K**	**298 K**	**308 K**	**318 K**	**(kJ mol^{-1})**	**(J $mol^{-1}K^{-1}$)**	**(kJ mol^{-1})**
H	5.94	5.35	4.70	4.03	12.3±0.5	20 ± 2	6.61±0.4
p-Me	6.15	5.51	4.88	4.23	11.9±0.4	18 ± 1	6.70±0.3
p-Ome	6.23	5.61	4.96	4.33	11.7±0.4	17 ± 1	6.74±0.3
p-Cl	5.98	5.36	4.70	4.06	12.3±0.4	20 ± 1	6.62±0.3
p-Br	5.45	4.83	4.17	2.59	13.1±0.4	23 ± 1	6.36±0.3
p-F	6.19	5.55	4.92	4.30	11.7±0.3	17 ± 1	6.72±0.3
p-NO_2	5.58	4.93	4.35	3.71	12.7±0.4	22 ± 2	6.43±0.4
p-COOMe	5.85	5.22	4.59	3.96	12.4±0.4	20 ± 1	6.56±0.3
p-NH_2	5.90	5.25	4.66	4.01	12.2±0.4	19 ± 1	6.59±0.3
p-COMe	5.33	4.71	4.05	3.45	13.6±0.5	25 ± 1	6.30±0.4
p-NHAc	5.45	4.80	4.21	3.56	13.2±0.5	23 ± 2	6.36±0.4
m-Me	6.03	5.41	4.75	4.14	12.1±0.4	19 ± 1	6.65±0.3

K/ (dm^3 mol^{-1})					$-\Delta H^*$	$-\Delta S^*$	$-\Delta G^*$
Substituent	**288 K**	**298 K**	**308 K**	**318 K**	**(kJ mol^{-1})**	**(J $mol^{-1}K^{-1}$)**	**(kJ mol^{-1})**
m-Ome	6.12	5.48	4.85	4.23	11.8±0.3	18 ± 1	6.69±0.3
m-Cl	6.00	5.35	4.73	4.10	12.3±0.6	19 ± 2	6.65±0.5
m-Br	5.44	4.80	4.21	3.57	13.1±0.5	23 ± 2	6.34±0.4
m-I	5.74	5.13	4.48	3.88	12.5±0.4	20 ± 1	6.51±0.3
m-NO_2	5.65	5.04	4.37	3.78	12.7±0.4	22 ± 1	6.46±0.3
m-CO_2Me	6.21	5.59	4.94	4.32	11.7±0.4	17 ± 1	6.73±0.3
o-Me	5.29	4.65	4.05	3.42	13.5±0.5	25 ± 2	6.28±0.4
o-OMe	5.54	4.90	4.29	3.66	12.9±0.4	22 ± 1	6.41±0.3
o-NO_2	5.33	4.70	4.05	3.45	13.5±0.4	25 ± 1	6.29±0.3
o-COOMe	6.01	5.37	4.76	4.13	12.0±0.4	18 ± 1	6.64±0.3
o-Cl	5.33	4.70	4.05	3.45	12.2±0.5	19 ± 2	6.61±0.4
o-Br	5.47	4.85	4.22	3.59	13.1±0.5	23 ± 2	6.37±0.4
o-I	6.07	5.42	4.80	4.21	11.8±0.3	18 ± 1	6.66±0.2
o-NH_2	5.96	5.35	4.73	4.03	12.3±0.6	20 ± 2	6.62±0.4
Alkyl phenyl sulfides							
Et	6.14	5.35	4.92	4.28	11.7±0.4	17±1	6.71±0.3
Pr	5.92	5.32	4.69	4.05	12.1±0.4	19±1	6.60±0.3
i-Pr	5.46	4.85	4.22	3.58	13.2±0.5	23±2	6.37±0.4
t-Bu	5.85	5.22	4.57	3.96	12.4±0.4	20±1	6.56±0.3
Other Sulfides							
Me_2S	5.63	5.02	4.35	3.75	12.8±0.4	22±1	6.45±0.3
Pr_2S	5.85	5.20	4.57	3.93	12.3±0.5	20±2	6.55±0.4
Ph_2S	5.76	5.15	4.53	3.89	12.5±0.4	20±1	6.53±0.3

3.2 Acryliconitrile Induced Polymerisation

Methyl phenyl sulphide oxidation in a nitrogen environment did not result in acryliconitrile polymerisation. Additionally, the oxidation rate was unaffected by the addition of acrylonitrile (Table 1). Hence, the formation of free radicals due to a one-electron oxidation is quite improbable.

3.3 Effect of Acidity

The reaction is catalysed by hydrogen ions (Table 4). The hydrogen-ion dependence has the form $k_{obs} = a + b[H^+]$. The values of a and bare $7.84\pm0.07\times 10^{-4}$ s^{-1} and $9.32\pm0.12\times10^{-4}$ mol^{-1} dm^3 s^{-1} respectively ($r^2 = 0.9994$).

3.4 Solvent Effect

The oxidation of methyl phenyl sulfide was studied in nineteen organic solvents. The choice of solvents was limited due to the solubility of DEACC and its reaction with primary and secondary alcohols. There was no reaction with the chosen solvents. The kinetics are similar in all the solvents. The values of K and k_2 are recorded in Table 5.

Table 4. Dependence of reaction rate on hydrogen ion concentration

[DEACC] = 0.001moldm^{-3};	**[MeSPh] = 0.10 moldm^{-3};**			**Temp. = 298K**		
$[H^+]$/moldm^3	0.10	0.20	0.40	0.60	0.80	1.00
$10^4 k_{obs}/s^{-1}$	8.73	9.63	11.7	13.5	15.3	17.1

Table 5. Effect of solvents on the oxidation of Benzaldehyde by DEACC at 308 K

Solvents	K (dm^{-3} mol^{-1})	10^5 k_2 (dm^3mol^{-1} s^{-1})	Solvents	K (dm^{-3} mol^{-1})	10^5 k_2 ($dm^3mol^{-1}s^{-1}$)
Chloroform	5.85	38.9	Toluene	4.99	6.46
1,2-Dichloroethane	4.55	33.9	Acetophenone	5.58	43.6
Dichloromethane	6.03	40.7	Tetrahydrofuran	5.88	12.0
DMSO	6.12	107	t-Butylalcohol	6.00	16.2
Acetone	5.25	31.6	1,4-Dioxane	5.66	14.8
DMF	5.35	56.7	1,2-Dimethoxyethane	5.55	7.94
Butanone	5.45	22.4	Carbondisulfide	4.82	2.82
Nitrobenzene	4.88	36.3	Acetic Acid	5.57	15.5
Benzene	5.55	9.55	Ethyl Acetate	5.58	11.5
Cyclohexane	4.47	1.51			

A significant correlation was observed between the activation enthalpies and entropies for the oxidation of thirty-three sulfides in dimethylformamide (DMF), with a correlation coefficient of r^2=0.8607, indicating the presence of an enthalpy–entropy compensation effect (Liu & Guo, 2001). The isokinetic temperature derived from this correlation, using the method proposed by Leffler (Leffler, 1955) and refined by Patterson (Petersen, 1964), was calculated to be 479 ± 35 K. To further validate the compensation effect, Exner's criterion was applied (Exner, 1964). A linear Exner plot of log k at 288 K versus 318 K yielded a high degree of correlation (r^2=0.993), with a slope of 0.8327±0.0122 (Fig. 3). The isokinetic temperature estimated from the Exner plot was 667 ± 64 K. The existence of a linear isokinetic relationship suggests that all thirty-three sulfides undergo oxidation through a common mechanistic pathway. Moreover, such a linear relationship is a necessary condition for the applicability of linear free energy relationships (LFERs). The Gibbs free energy of activation (ΔG^*) across the series was found to range from 82 to 97 kJ/mol. This variation corresponds to an approximately 200-fold difference in the observed reaction rates, underscoring the influence of structural variation on kinetic behaviour.

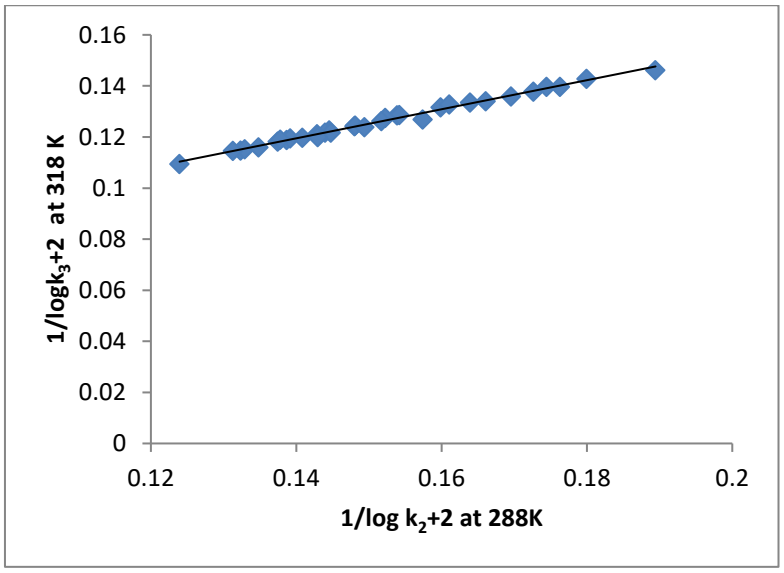


Fig. 3. Exner's Isokinetic relationship in the oxidation of sulfides by DEACC

3.5 Solvent Effect

The rate constants for oxidation, k_2, in eighteen solvents (excluding CS_2 due to incomplete solvent parameter data) were connected using the linear solvation energy relationship equation (Kamlet et al. 1983) in Equation (5).

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha \quad (5)$$

In this equation, π* denotes the solvent polarity, β signifies the hydrogen bond acceptor basicities, and α indicates the hydrogen bond donor acidity. A_0 represents the intercept phrase. It is noteworthy that of the 18 solvents, 12 have an outcome of zero for α. The results of correlation analyses in terms of equation (5), a biparametric equation involving π^* and β, and separately with π^* and β are given below.

$$\log k_2 = -4.05 + 1.88\ (\pm 0.21)\ \pi^* + 0.14\ (\pm 0.17)\ \beta + 0.31\ (\pm 0.16)\ \alpha \quad (6)$$
$R^2 = 0.8718;\ \ sd = 0.19;\ \ n = 18;\ \ \psi = 0.39$

$$\log k_2 = -4.02 + 1.77\ (\pm 0.21)\ \pi^* + 0.25\ (\pm 0.18)\ \beta \quad (7)$$

$R^2 = 0.8398;\ \ sd = 0.21;\ \ n = 18;\ \ \psi = 0.42$

$$\log k_2 = -4.07 + 1.84\ (\pm 0.22)\ \pi^* \quad (8)$$

$r^2 = 0.8136;\ \ sd = 0.21;\ \ n = 18;\ \ \psi = 0.44$

$$\log k_2 = -2.95 + 0.56\ (\pm 0.39)\ \beta \quad (9)$$

$r^2 = 0.1151;\ \ sd = 0.47;\ \ n = 18;\ \ \psi = 0.97$

The number of data points is denoted by n, and ψ represents Exner's statistical parameter (Exner, 1966). The solvent effect on the oxidation reaction was initially evaluated using Kamlet's triparametric equation, which accounts for approximately 87% of the observed variation in reaction rates. Despite this, the correlation does not meet the criteria for statistical significance when assessed using Exner's test (cf. Equation 6), suggesting that the triparametric model may not adequately describe the system.

The data on the solvent effect were analyzed in terms of Swain's equation of cation- and anion-solvating concept of the solvents as well (Swain et al. 1983).

$$\log k_2 = aA + bB + C \quad (10)$$

In this case, A stands for the solvent's anion solvating power and B for its cation solvating power. The intercept term is C. The solvent polarity is assumed to be represented by (A+B). Equation (10), independently of A and B and with (A + B), was used to assess the rates in various solvents.

$$\log k_2 = 1.37\ (\pm 0.04)\ A + 1.78\ (\pm 0.03)\ B - 4.31 \quad (11)$$

$R^2 = 0.9956;\ sd = 0.03;\ n = 19;\ \psi = 0.07$

$$\log k_2 = 1.12\ (\pm 0.59)\ A - 4.93 \quad (12)$$

$r^2 = 0.1769;\ sd = 0.47;\ n = 19;\ \psi = 0.93$

$$\log k_2 = 1.67\ (\pm 0.24)\ B - 4.53 \quad (13)$$

$r^2 = 0.7329;\ sd = 0.27;\ n = 19;\ \psi = 0.53$

$$\log k_2 = 1.64 \pm 0.06\ (A + B) - 4.29 \quad (14)$$

$r^2 = 0.9793;\ sd = 0.07;\ n = 19;\ \psi = 0.15$

Although the contribution of cation solvation was found to be slightly greater than that of anion solvation, both cationic and anionic solvation play significant roles in determining the rates of oxidation of methyl phenyl sulphide across different solvents. The observed rates exhibited excellent correlation with Swain's equation. Furthermore, approximately 98% of the variation in the reaction rates could be attributed to solvent polarity, as represented by the combined parameters (A + B), whereas individual correlations with A or B alone were negligible. An attempt was made to correlate the reaction rate with the solvent's relative permittivity, given that solvent polarity accounts for the majority of the observed data. However, a plot of log k2k_2k2 versus the reciprocal of relative permittivity was non-linear ($r^2 = 0.4603$; sd = 0.38; ψ = 0.75), indicating that relative permittivity alone does not adequately describe the solvent effect. The data suggest that the transition state is

more polar than the reactant state, consistent with the observed influence of solvent polarity on the reaction kinetics.

Furthermore, the significant contribution of both cation-solvating and anion-solvating powers indicates the creation of a dipolar transition state, akin to that of SN_2 reactions. It is also possible to explain the solvent effect by supposing that the oxidant and the intermediate complex are significantly dissociated in more polar solvents and exist as an ion pair in non-polar solvents like cyclohexane.

3.6 Reactivity Correlation Analysis

A review of the data in Tables 2 and 3 revealed that there is little variance in the intermediate complexes' formation constants, K. Nevertheless, the kind of substituent affects the disproportionation's rate constants, k_2. Thus, correlation analysis was performed on the rate constants, k_2. Aryl Methyl Sulphides: The Hammett equation (Johnson, 1980) and dual substituent parameter (DSP) equations (Swain et al. 1983) have been used to try to correlate the influence of substituents on reactivity.

A triparametric LDR equation for the quantitative result of substituent types' varying modes of electron delocalisation was presented by Charton (Charton, 1975) in the late 1980s. A distinct sensitivity to the electronic demand for the phenomena under study reflects this distinction. Because the same three substituent constants are said to encompass the whole spectrum of electrical effects of substituents, it has the benefit of not needing a choice of parameters. As a result, we have started using the LDR equation to investigate how structure affects reactivity. The LDR equation (15) has been applied to the rate constants, k_2, in this study.

$$\log k_2 = L\,\sigma_l + D\,\sigma_d + R\,\sigma_e + h \quad (15)$$

In this case, σ_l is a localized (field and/or inductive) effect parameter, σ_d is the intrinsic delocalized (resonance) electrical effect parameter when the active site doesn't need much electronic demand, and σ_e shows how sensitive the substituent is to changes in the active site's electronic demand. Equation (16) shows how the last two substituent parameters are connected.

$$\sigma_D = \eta\sigma_e + \sigma_d \quad (16)$$

Here η represents the electronic demand of the reaction site and is given by the relation $\eta = R/D$, and σ_D represents the delocalized electrical parameter of the diparametric LD equation.

For the ortho-substituted compounds, it is necessary to account for the possibility of steric effects and Charton therefore modified the LDR equation to generate the LDRS equation (17).

$$\log k_2 = L\,\sigma_l + D\,\sigma_d + R\,\sigma_e + S\,\upsilon + h \quad (17)$$

Where υ is the well-known Charton's steric parameter based on Van der Waals radii (Charton (1975).

The oxidation rates of *ortho*, *meta*, and *para*-substituted sulfides showed excellent correlations with the LDR and LDRS equations (Table 6). Notably, improved correlations were observed for *ortho*-substituents such as *o*-NO_2 and *o*-CO_2Me when their orthogonal conformations were considered. Goodness of fit was evaluated using standard deviation (sd), the coefficient of multiple determination (R^2), and Exner's statistical parameter (ψ).

A comparison of the *L* (localized) and *D* (delocalized) values revealed that *para*-substituted sulfides are more influenced by delocalization effects, whereas *meta*-substituted compounds are more affected by field (inductive) effects. The oxidation of *ortho*-substituted sulfides appears to be equally governed by both. In all cases, the reaction constants decreased with rising temperature, indicating reduced selectivity at higher temperatures.

An electron-deficient sulphurcentre in the transition state of the rate-determining step was indicated by the negative values of the three regression coefficients, L, D, and R. The positive value of e increases the substituent's ability to donate electrons and stabilise a cationic intermediate by contributing a negative increment to d (Equation 17).

Table 6. Impact of Temperature and Reactivity Trends in the Oxidation of Organic Sulfides by DEACC

T/K	- L	- D	- R	S	η	R^2	sd	Ψ	P_D	P_S
Para-substituted										
288	1.43	1.80	1.32	-	0.73	0.9998	0.005	0.02	44.3	-
298	1.36	1.71	1.28	-	0.75	0.9999	0.006	0.01	44.3	-
308	1.26	1.62	1.16	-	0.72	0.9989	0.005	0.04	43.7	-
318	1.19	1.54	1.01	-	0.66	0.9999	0.006	0.01	43.6	-
Meta-substituted										
288	1.80	1.44	1.31	-	0.91	0.9999	0.004	0.01	55.5	-
298	1.70	1.35	1.34	-	0.99	0.9998	0.009	0.02	55.7	-
308	1.61	1.27	1.11	-	0.87	0.9998	0.007	0.02	55.3	-
318	1.52	1.18	0.86	-	0.78	0.9998	0.007	0.02	56.3	-
Ortho-substituted										
288	1.55	1.62	1.30	1.16	0.80	0.9999	0.006	0.01	51.1	26.8
298	1.44	1.54	1.20	1.07	0.78	0.9998	0.007	0.02	51.2	26.4
308	1.35	1.43	1.13	0.99	0.79	0.9989	0.005	0.04	51.4	26.2
318	1.25	1.34	1.04	0.93	0.78	0.9998	0.009	0.02	51.7	26.4

The negative value of S indicates that the reaction is subjected to steric hindrance by the ortho-substituent. This may be due to the 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. (18)-(20)] showed that all four substituent constants are significant.

$$\log k_2 = -1.97\ (\pm 0.43)\sigma_l - 1.35\ (\pm 0.35)\sigma_d - 1.86\ (\pm 2.50)\sigma_e - 3.00 \quad (18)$$

$R^2 = 0.9092$, sd = 0.26, n = 10 Ψ = 0.37

$$\log k_2 = -1.89\ (\pm 0.45)\sigma_d + 0.61\ (\pm 3.20)\sigma_e - 1.74\ (\pm 0.55)\ \upsilon - 2.90 \quad (19)$$

$R^2 = 0.8445$, sd = 0.35, n = 10, Ψ = 0.48

$$\log k_2 = -2.14\ (\pm 0.88)\sigma_l - 5.33\ (\pm 4.41)\sigma_e - 0.60\ (\pm 0.88)\ \upsilon - 2.67 \quad (20)$$

$R^2 = 0.6734$, sd = 0.50, n = 10, Ψ = 0.70

Similarly, for the oxidation of *para*- and *meta*-substituted sulfides, multiple regression analyses confirm that both localized and delocalized electronic effects significantly influence the reaction rate. Importantly, no significant collinearity was observed among the substituent constants across the three substitution patterns.

A comparison of the reaction constants across the *ortho*, *meta*, and *para* series reveals insightful trends. At 293 K, the values of *L* are 1.64, 1.43, and 1.32, respectively—indicating a decreasing magnitude as the substituent moves further from the reactive centre. In contrast, the corresponding *D* values are 1.67, 1.25, and 1.66, showing that delocalization effects are nearly equal at *ortho* and *para* positions but significantly lower at the *meta* position. These trends are consistent with expected electronic transmission effects.

The percent contribution of the delocalized effect (P_D) was calculated using Charton's method (Charton, 1975), as expressed in Equation (21).

$$P_D = (|D| \times 100) / (|L| + |D|) \quad (21)$$

Similarly, the percent contribution of the steric parameter (Johnson,1980) to the total effect of the substituent, P_S, was determined by using equation (22).

$$P_S = (|S| \times 100) / (|L| + |D| + |S|) \quad (22)$$

The values of the percent delocalization (P_D) and steric (P_S) contributions are summarized in Table 6. For *para*-substituted sulfides, P_D is approximately 44%, while the corresponding values for *meta*- and *ortho*-substituted sulfides are about 55% and 51%, respectively. These differences reflect variations in the balance between localization and delocalization effects depending on the position of substitution. The relatively weaker resonance contribution from the *ortho* position, compared to *para*, may be attributed to steric hindrance causing the methyl thio group to twist out of the benzene ring plane, reducing conjugative overlap. The P_S values indicate that steric effects are significant, particularly for *ortho*-substituted compounds, further supporting the role of spatial constraints in modulating reactivity.

Previous studies on sulfide oxidations involving direct oxygen transfer via electrophilic attack at the sulfur center reported negative but moderate reaction constants, such as hydrogen peroxide (–1.13) (Modena & Maioli, (1957), periodate (–1.40) permanganate (–1.52) (Ruff & Kucsman, 1985). (Banerji, 1988), and peroxydisulfate (–0.56) (Srinivasan et al. 1978). In contrast, reactions involving halogeno-sulfonium cation intermediates showed significantly larger negative values, such as chloramine-T (–4.25) (Ruf& Kucsman,1975), bromine (–3.2), and *N*-bromoacetamide (–3.75) (Perumal et al. 1985). For the oxidation by *N*-chloroacetamide, the =field (ρ_I) and resonance (ρ_{R^+}) reaction constants at 298 K were –1.3 and –1.7, respectively (Agarwal et al. 1990).

Alkyl Phenyl Sulfides: The oxidation rates of alkyl phenyl sulfides showed no significant correlation when analyzed separately with Taft's σ^* or E_s values (*Pavelich & Taft, 1957).* Consequently, the data were evaluated using the dual substituent parameter (DSP) using equation (23).

$$\log k_2 = \rho^*\sigma^* + \delta E_s + \log k_0 \quad (23)$$

The correlations obtained using the DSP equation are excellent (Table 7). Although the number of compounds analyzed is limited to just five, the results offer valuable qualitative insights. The negative polar reaction constant indicates that electron-donating alkyl groups enhance the oxidation rate. In contrast, steric effects exert an inhibitory influence. The observed reactivity pattern in the oxidation of alkyl phenyl sulfides can be attributed to the effective competition between electronic and steric factors.

Table 7. Reactivity trends in alkyl phenyl sulfide oxidation via dual substituent parameter analysis by Pavelich and Taft equation

Temp./K	$-\rho^*$	δ	R^2	Sd	ψ
288	2.49±0.11	0.85±0.02	0.9995	0.011	0.05
298	2.68±0.06	0.80±0.01	0.9998	0.012	0.05
308	2.64±0.04	0.74±0.01	0.9999	0.021	0.10
318	2.57±0.14	0.63±0.02	0.9981	0.030	0.15

3.7 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 DEACC to give a stronger oxidant and electrophile (24).

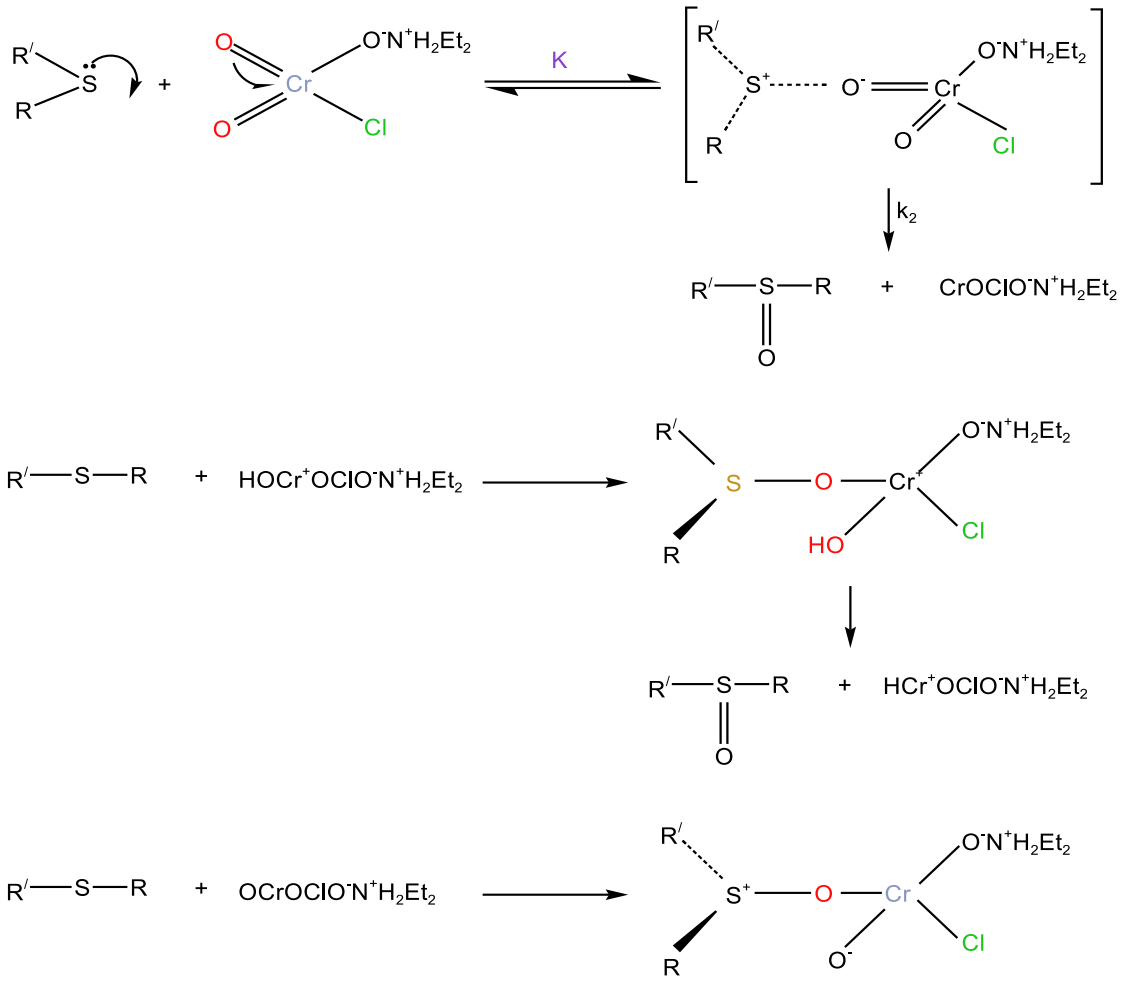
$$O_2CrClO^-N^+H_2Et_2 + TsOH \overset{+}{\leftrightarrows} [OCr(OH)ClO^- N^+H_2Et_2]^+ [TsO]^- \quad (24)$$

Since TsOH is a strong acid, it should be strongly ionised in a polar, aprotic solvent such as DMSO. Nonetheless, the production of an ion pair cannot be completely ruled out. As a result, the ion pair may be the reactive oxidising species in the catalysed process. It has been proposed that TsOH and immidazolium dichromate (IDC) form a complex (Karunakaran & Chidambaranathan, 1998). Although no spectra are given in the study, it has been asserted that there are spectral evidences. The authors have asserted a Michaelis-Menten type of kinetics with regard to TsOH based on a mere threefold change in [TsOH]. The reliance on TsOH, however, also takes the form $k_{obs} = a + b$ [TsOH] in that instance, according to a least-squares analysis of their data, with a = = 2.53±0.09 × 10^{-4} s^{-1}, b = 4.46 ± 0.15 × 10^{-4} mol^{-1} dm^3 s^{-1}, and r^2 = 0.9955. Either the protonated Cr (VI) molecule or an ion-pair of the protonated Cr (VI) and tosylate ion might be the species.

The transition state is more polar than the reactants, according to the examination of the solvent effect. Furthermore, the solvents' significant involvement in solvating both cations and anion implies that a substantial amount of charge separation occurs during the rate-determining stage.

The experimental observations can be interpreted in terms of electrophilic oxygen transfer from DEACC to the sulfide via an intermediate complex (Scheme 1), analogous to mechanisms proposed for the oxidation of sulfides and iodide ions by periodate (Indelli *et al.*, 1966), the oxidation of sulfides by hydrogen peroxide and by perfluorochromates (Banerji, 1988). The relatively low values of the polar reaction constants are consistent with the formation of a polar transition state in the rate-determining step. Electrophilic attack at the sulfide sulfur is further supported by the positive Hammett substituent constant (η), indicating that substituents capable of stabilising a cationic or electron-deficient site accelerate the reaction.

The modest magnitude of η, reflecting the electronic demand of the reaction, suggests limited charge separation in the transition state, supporting a mechanism involving a polar intermediate. By comparison, the formation of a positively charged sulfonium cation during oxidation by Cl^+ is more sensitive to steric effects than observed in the present study (Ruff *et al.*, 1975). The observed solvent effects also indicate a transition state that is more polar than the reactants, consistent with an SN2-like character in the rate-determining step. Collectively, the kinetic and mechanistic evidence supports an oxidation pathway proceeding via a polar, electrophilic transition state with limited charge separation, mediated by an intermediate complex.

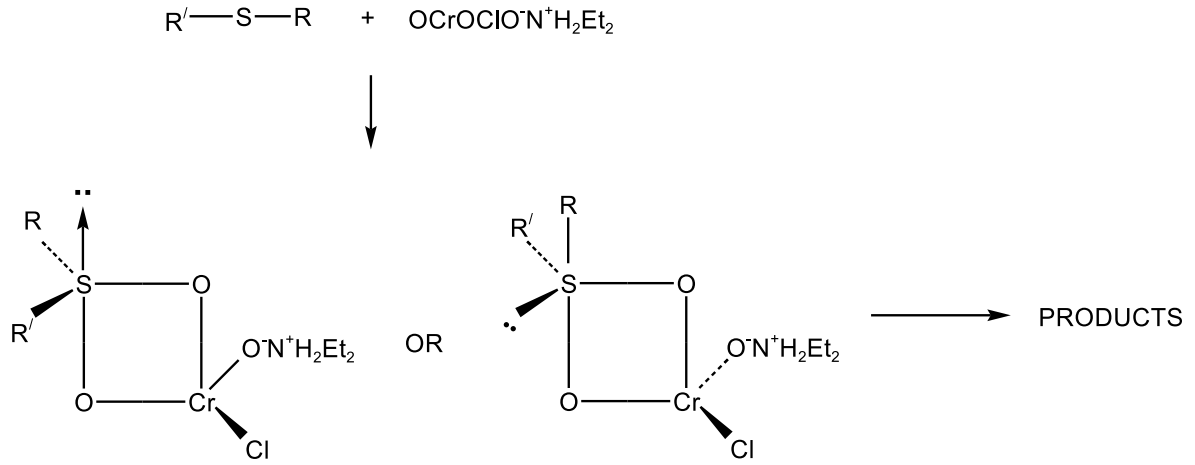


Scheme 1. Electrophilic oxygen transfer from DEACC to the sulfide *via* an intermediate complex

The oxidation of sulfides by DEACC has been proposed to potentially proceed via a cyclic intermediate, as observed in various reactions of Cr(VI) species (Chang & Westheimer, 1960). In this pathway, the cyclic

transition state would experience significant strain due to the apical positioning of a lone pair or an alkyl group (Scheme 2). The steric demands associated with such a cyclic mechanism are considerably higher than those suggested in Scheme 1. Accordingly, the relatively small values of the steric reaction constants observed experimentally are more consistent with an acyclic mechanistic pathway.

Formation of a cyclic transition state would require a precise spatial orientation of reactants and is expected to result in a significantly more negative entropy of activation than what is experimentally observed. In this study, the measured entropy of activation is comparable to values reported for typical oxygen-transfer reactions, including the oxidation of iodide ions by periodate (Ruff & Kucsman, 1985) and the oxidation of methyl phenyl sulfide (MeSPh) by hydrogen peroxide, periodate (Ruff et al., 1975), and perfluorochromates (Banerji, 1988). These observations support an acyclic transition state for the DEACC-mediated oxidation of sulfides. (ΔS^* = –96, –115, –113, and –89 J mol^{-1} K^{-1} respectively). In the oxidation of vicinal-diols by chromic acid, where formation of a cyclic transition state has been proposed, Chatterjee and Mukherji obtained entropies of activation in the range of –174 to –195 J mol^{-1} K^{-1} (Chatterji & Mukherjee, 1957).



Scheme 2. The cyclic transition in view of the apical position of a lone pair of electrons or an alkyl group

It is noteworthy to compare the oxidation of organic sulfides by perfluorochromates (PFC) (Panigrahi & Mahapatro, 1981), pyridinium chlorochromate (PCC) (Panigrahi & Mahapatro, 1981), pyridinium bromochromate (PBC) (Loonker *et al.*, 1997), and DEACC. Oxidation by PFC and PBC exhibited similar kinetic behaviour, with the reactions being first order with respect to the reductant. In contrast, oxidation by PCC and DEACC followed Michaelis–Menten-type kinetics with respect to the reductant. One plausible explanation is that the formation constants of the reductant–PFC/PBC complexes are very low, leading to apparent second-order kinetics, although a definitive explanation for this discrepancy remains elusive. Solvent effects (not investigated for PCC oxidation) and the influence of hydrogen ion concentration appear to be comparable across these reactions, supporting the proposition of essentially analogous mechanistic pathways for sulfide oxidation mediated by these Cr(VI) reagents.

4. Conclusion

The oxidation of alkyl phenyl sulphides by diethylammonium chlorochromate depends on both electronic and steric effects of the substituents and proceeds through electrophilic oxygen transfer from oxidant to sulphide in the rate-determining step. Positive values of η, which represent the electronic demand of the reaction, indicate a less severe charge separation in the transition state. Even with a few chemicals, the Pavelich–Taft DSP equation demonstrated good correlation. The negative polar reaction constant shows that electron-donating alkyl groups stabilise the transition state and aid oxidation. Bulkier substituents' steric hindrance slows the reaction rate, demonstrating the spatial effects' inhibitory impact. These results show that electronic facilitation and steric inhibition compete to control reactivity. Although the dataset is tiny, the DSP analysis provides qualitative insight into the reaction's mechanistic aspects and supports the use of multiparametric models to understand substituent effects in organic oxidation processes.

Disclaimer (Artificial Intelligence)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc.) and text-to-image generators have been used during the writing or editing of this manuscript.

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Competing Interests

Authors have declared that no competing interests exist.

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