Kinetics and Mechanism of the Oxidation of Some Organic Sulfides by Morpholinium Chlorochromate

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Received 11 January 2008; revised 13 June 2008; accepted 26 June 2008

DOI 10.1002/kin.20372 Published online in Wiley InterScience (www.interscience.wiley.com).

> ABSTRACT: The oxidation of organic sulfides by morpholinium chlorochromate (MCC) resulted in the formation of the corresponding sulfoxides. The reaction is first order with respect to both MCC and the sulfide. The reaction is catalyzed by toluene-*p*-sulfonic acid (TsOH). The oxidation was studied in 19 different organic solvents. An analysis of the solvent effect by Swain's equation showed that both the cation- and anion-solvating powers of the solvents play important roles. The correlation analyses of the rate of oxidation of 34 sulfides were performed in terms of various single and multiparametric equations. For the aryl methyl sulfides, the best correlation is obtained with Charton's localized-delocalized-resonance and localized-delocalized-resonancesteric equations. The oxidation of alkyl phenyl sulfides exhibited a very good correlation in terms of the Pavelich–Taft equation. The polar reaction constants are negative, indicating an electrondeficient sulfur center in the rate-determining step. A mechanism involving formation of a sulfonium cation intermediate in the slow step has been proposed. © 2008 Wiley Periodicals, Inc. Int J Chem Kinet 41: 65–72, 2009

INTRODUCTION

Pyridinium and quinolinium halochromates have long been used as mild and selective oxidizing reagents in synthetic organic chemistry [1–5]. Morpholinium chlorochromate (MCC) is one such compound used for the oxidation of primary aliphatic alcohols [6]. There

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seem to be only a few reports on the oxidation aspects, using MCC emanated from our laboratory [7,8]. However, the kinetics of oxidation of organic sulfides by MCC has not been investigated. We have been interested in the kinetic and mechanistic aspects of the oxidation by complexed Cr(VI) species, and some reports have already been published [9]. Karunakaran et al. [10] have reported a common mechanism for the oxidation of diphenyl sulfide by various Cr(VI) reagents in acetic acid. In the present article, we report the kinetics of oxidation of 34 organic sulfides by MCC in dimethylsulfoxide (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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Contract grant sponsor: Council of Scientific and Industrial Research, New Delhi, India.

Contract grant number: 01/(2014)/05/EMR-II.

EXPERIMENTAL

Materials

The sulfides were either commercial products or prepared by known methods [11] and were purified by distillation under reduced pressure or crystallization. Their purity was checked by comparing their boiling or melting point with the literature values. MCC was prepared by the reported method [6]. Toluene-*p*-sulfonic acid (TsOH) was used as a source of hydrogen ions.

Product Analysis

MeSPh or Me₂S (0.1 mol) and MCC (0.01 mol) were dissolved in DMSO (50 mL), and the mixture was allowed to stand for ca. 20 h. Most of the solvent was removed under reduced pressure. The residue was diluted with water and extracted with chloroform $(3 \times 50 \text{ mL})$. The chloroform layer was dried over anhydrous magnesium sulfate, the solvent was removed by evaporation, and the residue was analyzed by IR and ¹H NMR spectroscopy. The spectra were identical to those of the corresponding sulfoxides. Peaks characteristic of the sulfide and sulfone could not be detected. In IR spectra, the product showed a strong and broad absorption at 1050 cm⁻¹. No band either at 1330 or 1135 cm⁻¹, characteristic of sulfones [12] was seen. In NMR spectroscopy studied in the case of Me₂S, the peak due to methyl protons shifted from 2.1 τ , in the sulfide, to 2.6 τ in the product. In the corresponding sulfone, the peak should have appeared at 3.0 τ [13]. 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 3.95 ± 0.1 .

Kinetic Measurements

The reactions were studied under pseudo-first-order conditions by keeping an excess (×15 or greater) of the sulfide over MCC. 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 MCC at 350 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 [MCC] against time. Duplicate kinetic runs 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 computed from the relation

 $k_2 = k_{obs}/[sulfide]$. Simple and multivariate regression analyses were carried out by the least-squares method.

RESULTS

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

$$\begin{array}{rcl} \text{R-S-R'} + \text{CrO}_2\text{ClOMH} & \rightarrow & \text{R-S-R'} + \text{CrOClOMH} & (1) \\ & & \text{O} \end{array}$$

MCC undergoes a two-electron change. This is according to the earlier observations with MCC [7,8] and with structurally similar other halochromates [9]. It has already been shown that both pyridinium fluorochromate (PFC) [14] and pyridinium chlorochromate (PCC) [15] 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 IR studies.

Rate Law

The reactions were found to be first order with respect to MCC. The individual kinetic runs were strictly first order to MCC. Furthermore, the first-order rate coefficients did not vary with the initial concentration of MCC. The order with respect to sulfide was also found to be one (Table I).

 Table I
 Rate Constants for the Oxidation of Methyl

 Phenyl Sulfide by MCC at 298 K

10^{3} [MCC] (mol dm ⁻³)	[MeSPh] (mol dm ⁻³)	$[H^+]$ (mol dm ⁻³)	$10^{6} k_{obs}$ (s ⁻¹)
1.0	0.10	0.0	2.31
1.0	0.20	0.0	4.70
1.0	0.40	0.0	9.45
1.0	0.60	0.0	14.4
1.0	0.80	0.0	18.9
1.0	1.00	0.0	23.6
2.0	0.20	0.0	4.95
4.0	0.20	0.0	4.32
6.0	0.20	0.0	5.04
8.0	0.20	0.0	4.50
1.0	0.10	0.1	2.59
1.0	0.10	0.2	3.02
1.0	0.10	0.4	3.75
1.0	0.10	0.6	4.41
1.0	0.10	0.8	5.29
1.0	0.10	1.0	6.16
1.0	0.40^{a}	0.0	9.81 ^a

^aContained 0.001 mol dm⁻³ acrylonitrile.

Test for Free Radicals. The oxidation of methyl phenyl sulfide, in an atmosphere of nitrogen, failed to induce the polymerization of acrylonitrile. Furthermore, the addition of acrylonitrile had no effect on the rate of oxidation (Table I). To further confirm the absence of free radicals in the reaction pathway, the reaction was carried out in the presence of 0.05 mol dm⁻³ of 2,6-di-*t*-butyl-4-methylphenol (butylated hydroxytoluene or BHT). It was observed that BHT was recovered unchanged, almost quantitatively.

Effect of Substituents. The rates of oxidation of a number of ortho-, meta-, and parasubstituted phenyl methyl sulfides, alkyl phenyl sulfides, dialkyl sulfides, and diphenyl sulfide were determined at different tem-

peratures, and the activation parameters were calculated (Table II).

Effect of Acidity. The reaction is catalyzed by TsOH (Table I). The TsOH-dependence has the form $k_{obs} = a + b$ [TsOH]. The values of a and b are $2.91 \pm 0.06 \pm 10^{-4} \text{ s}^{-1}$ and $3.89 \pm 0.09 \pm 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, respectively ($r^2 = 0.9976$). Therefore, the experimental rate law has the following form:

Rate =

 k_2 [MCC][sulfide] + k_3 [MCC][sulfide][TsOH] (2)

Table II Rate Constants and Activation Parameters of the Oxidation of Organic Sulfides by MCC

		$10^5 k_2 (dm^3)$	$mol^{-1} s^{-1}$		ΔH^*	ΔS^*	ΔG^*
Substance	288 K	298 K	308 K	318 K	$(kJ mol^{-1})$	$(J \text{ mol}^{-1} \text{ K}^{-1})$	$(kJ mol^{-1})$
Н	11.7	23.6	47.7	95.4	50.7 ± 0.7	-125 ± 2	87.9 ± 0.5
<i>p</i> -Me	25.1	48.6	95.0	180	47.6 ± 0.6	-130 ± 2	86.2 ± 0.4
<i>p</i> -Ome	56.7	108	203	378	45.8 ± 0.4	-129 ± 1	84.2 ± 0.3
<i>p</i> -F	12.1	24.7	51.0	99.9	51.2 ± 0.5	-123 ± 1	87.8 ± 0.4
p-Cl	7.83	16.5	34.7	71.1	53.5 ± 0.5	-119 ± 2	88.8 ± 0.4
$p-NO_2$	0.68	1.60	3.84	9.02	63.1 ± 0.8	-106 ± 3	94.6 ± 0.6
<i>p</i> -COMe	1.71	3.83	8.55	18.9	58.4 ± 0.7	-115 ± 2	92.5 ± 0.6
<i>p</i> -COOMe	2.49	5.47	12.0	26.1	57.1 ± 0.8	-116 ± 2	91.6 ± 0.6
<i>p</i> -Br	7.74	16.2	34.1	70.2	53.4 ± 0.7	-119 ± 2	88.9 ± 0.5
<i>p</i> -NHAc	27.9	55.2	108	207	48.3 ± 0.5	-126 ± 2	85.9 ± 0.4
p-NH ₂	207	365	647	1130	40.6 ± 0.5	-137 ± 2	81.2 ± 0.4
<i>m</i> -Me	22.0	42.3	83.3	160	47.9 ± 0.7	-130 ± 2	86.5 ± 0.5
<i>m</i> -Ome	25.2	47.7	90.2	169	48.5 ± 0.6	-136 ± 2	86.2 ± 0.5
<i>m</i> -Cl	3.81	8.01	16.7	34.2	53.2 ± 0.6	-126 ± 2	90.6 ± 0.4
<i>m</i> -Br	3.75	7.83	16.2	33.3	52.9 ± 0.6	-127 ± 2	90.7 ± 0.5
<i>m</i> -I	4.56	9.45	19.8	40.5	52.9 ± 0.7	-125 ± 2	90.2 ± 0.5
$m-NO_2$	0.37	0.88	2.09	4.86	62.8 ± 0.7	-112 ± 2	96.1 ± 0.6
<i>m</i> -CO ₂ Me	1.91	4.23	9.31	19.8	56.9 ± 0.5	-112 ± 2	96.1 ± 0.6
o-Me	6.03	13.2	28.2	61.2	56.2 ± 0.8	-112 ± 3	89.4 ± 0.6
o-Ome	18.0	37.5	76.5	153	51.8 ± 0.4	-118 ± 1	86.8 ± 0.4
o-NO ₂	0.18	0.49	1.25	3.15	69.9 ± 0.5	-93 ± 2	97.6 ± 0.4
o-COOMe	0.54	1.32	3.22	7.74	65.0 ± 0.8	-101 ± 3	95.1 ± 0.6
o-Cl	1.44	3.42	8.10	18.0	61.7 ± 0.4	-105 ± 1	92.7 ± 0.3
o-Br	1.08	2.61	6.30	14.4	63.3 ± 0.5	-101 ± 2	93.4 ± 0.4
<i>o</i> -I	0.85	2.07	5.13	11.7	64.3 ± 0.6	-100 ± 2	93.9 ± 0.5
o-NH ₂	69.3	131	251	468	46.0 ± 0.6	-127 ± 2	83.7 ± 0.5
			Alk	yl Phenyl Sulf	ides		
Et	19.3	38.3	76.9	144	48.6 ± 0.4	-128 ± 1	86.8 ± 0.3
Pr	11.6	23.8	49.5	98.1	51.8 ± 0.5	-122 ± 2	87.9 ± 0.4
<i>i</i> -Pr	14.4	30.6	63.0	126	52.5 ± 0.3	-117 ± 1	87.3 ± 0.2
t-Bu	3.31	7.47	17.1	37.8	59.4 ± 0.7	-106 ± 2	90.8 ± 0.6
				Other Sulfides	3		
Me ₂ S	25.6	48.6	96.3	188	48.2 ± 0.9	-128 ± 3	86.1 ± 0.7
Pr ₂ S	44.1	81.9	153	280	44.4 ± 0.6	-136 ± 2	84.9 ± 0.4
Ph ₂ S	5.67	12.1	25.2	54.0	54.6 ± 0.7	-118 ± 2	89.6 ± 0.6

	$10^{6} k_{2}$		$10^{6} k_{2}$
Solvent	(s^{-1})	Solvent	(s^{-1})
Chloroform	17.8	Toluene	3.47
1,2-Dichloroethane	14.8	Acetophenone	18.2
Dichloromethane	16.2	Tetrahydrofuran	6.46
Dimethyl sulfoxide	47.7	t-Butyl alcohol	7.94
Acetone	12.6	1,4-Dioxane	6.17
DMF	22.9	1,2-Dimethoxyethane	3.89
Butanone	10.5	Ethyl acetate	5.25
Nitrobenzene	19.5	Carbon disulfide	1.86
Benzene	4.27	Acetic acid	7.08
Cyclohexane	0.44		

Table III Solvent Effect on the Oxidation of MeSPh by MCC at 308 K

Effect of Solvent. The oxidation of methyl phenyl sulfide was studied in 19 different organic solvents. The choice of solvent was limited by the solubility of MCC and its reaction with primary and secondary alcohols. There was no reaction with the solvent chosen. The kinetics were similar in all the solvents. The values of k_2 are recorded in Table III.

DISCUSSION

There is a fair correlation between the activation enthalpies and entropies of the oxidation of the 34 sulfides $(r^2 = 0.9569)$, indicating the operation of a compensation effect [16]. A correlation between the calculated values of enthalpies and entropies is often vitiated by the experimental errors associated with them. The reaction, however, exhibited an excellent isokinetic relationship, as determined by Exner's method [17]. An Exner plot between log k_2 at 288 K and at 318 K was linear $(r^2 = 0.9989, SD = 0.01, slope = 0.8401)$. The value of isokinetic temperature evaluated from the Exner's plot is 706 ± 50 K. The linear isokinetic correlation implies that all the sulfides are oxidized by the same mechanism, and the change in the rate of oxidation is governed by changes in both the enthalpy and entropy of the activation.

Solvent Effect

The correlation of rate constants for oxidation, k_2 , in 18 solvents (CS₂ was not considered, as the complete range of solvent parameters was not available) in terms of the linear solvation energy relationship (3) of Kamlet et al. [18] is not much significant ($R^2 = 0.8946$). The major contribution is of solvent polarity term, represented by π^* (4)

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha \tag{3}$$

$$\log k_2 = -5.74 + 1.82 \,(\pm 0.20) \pi^* \tag{4}$$

$$R^2 = 0.8312; SD = 0.20; n = 18; \psi = 0.31$$

We have used the standard deviation (SD), the coefficient of multiple determination (R^2), and Exner's [19] parameter, ψ , as the measures of goodness of fit. Here *n* is the number of data points.

The data on the solvent effect were analyzed in terms of Swain's equation [20] of cation- and anion-solvating concepts of the solvents as well.

$$\log k_2 = aA + bB + C \tag{5}$$

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 Eq. (5), separately with A and B and with (A + B).

$$\log k_2 = 1.37(\pm 0.03)A + 1.70(\pm 0.02)B - 6.08 (6)$$

$$R^2 = 0.9983; SD = 0.02; n = 19; \psi = 0.03$$

$$\log k_2 = 1.13(\pm 0.56)A - 4.91 (7)$$

$$R^2 = 0.1917; SD = 0.45; n = 19; \psi = 0.77$$

$$\log k_2 = 1.60(\pm 0.24)B - 5.63 (8)$$

$$R^2 = 0.7186; SD = 0.27; n = 19; \psi = 0.40$$

$$\log k_2 = 1.59 \pm 0.05(A + B) - 6.07 (9)$$

$$R^2 = 0.9863; SD = 0.06; n = 19; \psi = 0.09$$

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 anionsolvating 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. 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 ($r^2 = 0.5983$; SD = 0.32; $\psi = 0.49$).

Correlation Analysis of Reactivity

The data in Table II show that the oxidation of different sulfides follows the order of their nucleophilicity: $Pr_2S > Me_2S > Me_2S > Me_2S$. Aryl Methyl Sulfides. The correlation of the effect of substituents on the reactivity has been widely attempted in terms of the Hammett equation [21] or with dual substituent-parameter equations [22,23]. In the late 1980s, Charton [24] introduced a triparametric localized-delocalized-resonance (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 (10) to the rate constants, k_2 .

$$\log k_2 = L\sigma_{\rm l} + D\sigma_{\rm d} + R\sigma_{\rm e} + h \tag{10}$$

Here σ_1 is a localized (field and/or inductive) effect parameter, σ_d is the intrinsic-delocalized (resonance) electrical effect parameter when active site electronic demand is minimal, and σ_e represents the sensitivity of the substituent to changes in electronic demand by the active site. The latter two substituent parameters are related by Eq. (11).

$$\sigma_{\rm D} = \eta \sigma_{\rm e} + \sigma_{\rm d} \tag{11}$$

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

For orthosubstituted compounds, it is necessary to account for the possibility of steric effects and Charton [24], therefore, modified the LDR equation to generate the localized-delocalized-resonance-steric (LDRS) equation (12).

$$\log k_2 = L\sigma_l + D\sigma_d + R\sigma_e + S\upsilon + h \tag{12}$$

where v is the well-known Charton's steric parameter based on Van der Waals radii [25].

The rates of oxidation of ortho-, meta-, and parasubstituted sulfides show excellent correlations in terms of the LDR/LDRS equations (Table IV). The values of the independent variables, σ_1 , σ_d , σ_e , and υ were obtained from the work of Charton and Charton [24]. Although the number of data points is smaller than the optimum number, the correlations are excellent as per Exner's [19] 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 Eq. (12), 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 orthosubstituent. This may be due to steric hindrance of the orthosubstituent to the approach of the oxidizing species.

The percent contribution [25] of the delocalized effect, P_D is given by the following equation:

$$P_{\rm D} = (|D| \times 100) / (|L| + |D| + |R|)$$
(13)

	1	1					0		5	
T (K)	L	D	R	S	η	R^2	SD	ψ	$P_{\rm D}$	$P_{\rm S}$
				Para	substituted					
288	-1.53	-1.89	-1.69	_	0.89	0.9999	0.003	0.01	37.0	_
298	-1.44	-1.80	-1.62	_	0.90	0.9998	0.001	0.01	37.0	_
308	-1.35	-1.71	-1.52	_	0.89	0.9998	0.002	0.01	37.3	_
318	-1.26	-1.61	-1.51	_	0.93	0.9999	0.004	0.01	36.8	_
				Meta	substituted					
288	-1.98	-1.53	-1.33	_	0.87	0.9999	0.001	0.01	31.6	_
298	-1.89	-1.44	-1.25	_	0.86	0.9998	0.002	0.02	31.4	_
308	-1.81	-1.35	-1.23	_	0.91	0.9999	0.003	0.01	30.8	_
318	-1.73	-1.27	-1.10	_	0.87	0.9998	0.004	0.02	31.0	_
				Ortho	substituted	l				
288	-1.45	-1.55	-1.26	-1.13	0.81	0.9997	0.016	0.02	36.4	21.0
298	-1.40	-1.49	-1.20	-1.05	0.81	0.9999	0.002	0.01	36.4	20.4
308	-1.33	-1.41	-1.17	-0.99	0.83	0.9998	0.003	0.01	36.1	20.2
318	-1.26	-1.33	-1.10	-0.96	0.87	0.9997	0.015	0.02	36.0	20.6

Table IV Temperature Dependence for the Reaction Constants for the Oxidation of Organic Sulfides by MCC

Similarly, the percent contribution of the steric parameter [25] to the total effect of the substituent, P_S , was determined by using Eq. (14).

$$P_{\rm S} = (|S| \times 100) / (|L| + |D| + |S| + |R|)$$
(14)

The values of $P_{\rm D}$ and $P_{\rm S}$ are also recorded in Table IV. The value of $P_{\rm D}$ for the oxidation of parasubstituted sulfides is ca. 52%, whereas the corresponding values for the meta- and orthosubstituted aldehydes are ca. 39% and 49%, respectively. The less pronounced resonance effect from the orthoposition than from the paraposition may be due to the twisting away of the methylthio group from the plane of the benzene ring.

In earlier studies on the oxidations of sulfides, involving a direct oxygen transfer via an electrophilic attack on the sulfide–sulfur, the reaction constants were negative but of relatively small magnitude, for example, by hydrogen peroxide (-1.13) [26], periodate (-1.40) [27], permanganate (-1.52) [28], and peroxydisulfate (-0.56) [29]. Large negative reaction constants were exhibited by oxidations involving formation of halogeno-sulfonium cations, for example, by chloramine-T (-4.25) [30], bromine (-3.2) [31], and *N*-bromoacetamide (-3.75) [32]. In the oxidation by *N*-chloroacetamide (NCA) [33], the values of field ($\rho_{\rm I}$) and resonance ($\rho_{\rm R}^+$) 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 [34] dual substituent-parameter (DSP) equation (15).

$$\log k_2 = \rho^* \sigma^* + \delta E_s + \log K_0 \tag{15}$$

The correlations are excellent (Table V). Although 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 VCorrelation of Rate of Oxidation of AlkylPhenyl Sulfides with Pavelich-Taft Equation^a

Temperature (K)	$ ho^*$	δ	R^2	SD
288	-2.80 ± 0.01	0.90 ± 0.01	0.9999	0.01
298	-2.69 ± 0.01	0.85 ± 0.01	0.9998	0.02
308	-2.61 ± 0.02	0.80 ± 0.01	0.9999	0.01
318	-2.41 ± 0.09	0.73 ± 0.02	0.9993	0.03

^{*a*}No. of data points = 5.

Mechanisms

The observed dependence on TsOH suggests that the reaction follows two mechanistic pathways, one TsOH catalyzed and the other uncatalyzed. The catalytic effect of TsOH can be attributed to a protonation of MCC to give a stronger oxidant and electrophile (16).

bpyHOCrO₂Cl + TsOH

$$≈$$
 [bpyHOCr(OH)OCl]⁺[TsO]⁻ (16)

TsOH is a strong acid and is expected to be highly ionized in an aprotic polar solvent like DMSO. However, one cannot rule out the possibility of the formation of an ion pair. Therefore, the reactive oxidizing species in the catalyzed reaction may well be the ion pair. Formation of a complex between immidazolium dichromate (IDC) and TsOH has been suggested [35]. It has been claimed that there are spectral evidences, but no spectra have been included in the paper. On the basis of only a threefold variation in [TsOH], the authors have claimed a Michaelis-Menten type of kinetics with respect to TsOH. However, a least-squares analysis of their data indicated that in that case also, the dependence on TsOH has the form $k_{\text{obs}} = a + b$ [TsOH] with $a = 1.78 \pm 0.16 \times 10^{-3} \text{ s}^{-1}$, $b = 7.8 \pm 0.6 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, and $r^2 = 0.9809$. The species could be either the protonated Cr(VI) compound or an ion pair of the protonated Cr(VI) and tosylate ion.

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

The experimental results can be accounted for in terms of rate-determining electrophilic oxygen transfer from MCC to the sulfide as Eqs. (17) and (18), similar to that suggested for oxidations of sulfides and iodide ions by periodate ion [36] and for the oxidation of sulfides by hydrogen peroxide [26] and PFC [6]. The nucleophilic attack of a sulfide-sulfur on an MCC-oxygen may be viewed as an S_N2 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 sulfonium center as depicted in Eq. (19). Furthermore, an electrophilic attack on the sulfide-sulfur is confirmed by the positive value of η , which indicates that the substituent is able to stabilize a cationic or electron-deficient site. The low magnitude of η , 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 sulfonium cation and rather supports a mechanism involving the formation of a polar transition state in the rate-determining step. The formation of a positive sulfonium cation, in the oxidation of sulfides by Cl^+ , [37] is more responsive to steric hindrance than observed in the present study. The observed solvent effect also supports an S_N 2-like transition state.

than those of reaction (17), 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. The value of the entropy of activation obtained in this reaction is close to the value observed in typical





The oxidation of sulfides by MCC 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 reaction (20). The steric requirements of reaction (20) will be higher reactions involving oxygen transfer, for example, oxidation of iodide ion by periodate [36] and that of MeSPh by hydrogen peroxide [27], periodate [28], and PFC [39] ($\Delta S^* = -96$, -115, -113, and -89 J mol⁻¹ K⁻¹, respectively). In the oxidation of vicinal-diols by chromic acid, in which formation of a cyclic transition state has been proposed, Chatterjee and Mukherji [40] obtained entropies of activation in the range from -174 to -195 J mol⁻¹ K⁻¹.



It is of interest to compare here the mode of oxidation of organic sulfides by PFC [39], PCC [41], pyridinium bromochromate (PBC) [42], and MCC. The oxidation by PFC, PBC, and MCC presented a similar kinetic picture, that is, the reactions are of first order with respect to the reductants. In the oxidation by PCC a Michaelis-Menten type of kinetics was observed with respect to the reductants. It is possible that the values of the formation constants for the reductant-MCC complexes are very low. This resulted in the observation of second-order kinetics. No explanation of the difference is available presently. Solvent effects (in the oxidation by PCC, the effect of different solvents was not studied) and the dependence on TsOH are of similar nature in all these reactions, for which essentially similar mechanisms have been proposed. The common mechanism proposed [8] for the oxidation of diphenyl sulfide by Cr(VI) reagents, in acetic acid, is essentially similar to one proposed by us here.

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