MECHANISM OF THE OXIDATION OF ORGANIC SULPHIDES BY PERMANGANATE ION

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Abstract - The kinetics of the oxidation of number of aryl methyl, alkyl phenyl, dialkyl and diphenyl sulphides by permanganate ion to yield the sulphoxides, have been studied. The reaction is first order with respect to the sulphide and permanganate and is independent of hydrogen ion concentration. The reaction exhibited negative polar reaction constants and a small degree of steric hindrance. The lack of solvent isotope effect and the observed solvent effect (m = 0.39 for MeSPh) are explained by an electrophilic attack of permanganate-oxygen on the sulphide yielding a polar transition state. A moderate anchimeric assistance was observed in the oxidation of <u>o</u>-COOMe and <u>o</u>-COOH substituted methyl phenyl sulphide. A mechanism involving a one-step electrophilic oxygen transfer from permanganate ion to the sulphide and a polar product-like transition state, has been proposed.

The mechanism of the oxidation of sulphides to sulphoxides by many oxidants have been studied The mechanism depends largely on the nature of the oxidant. Halogenating agents convert sulphides into halogeno-sulphonium ions.^{1,2} The oxidations by peroxo ions,³ pyridinium chlorochromate,⁴ phenyliodoso diacetate,⁵ and chromic acid⁶ are proposed to involve intermediates with a sulphonium centre. In these reactions, sulphoxides are formed from the sulphonium intermediate in a subsequent step by a nucleophilic attack of water on the positively charged sulphur atom. Mechanisms involving the formation of sulphurane intermediates have been proposed in the oxidations by peroxyhexanoyl nitrate ⁷ and periodate ions.⁸ The permanganate ion oxidation of sulphides has been used in syntheses,⁹ but the reaction pathway has not been studied in detail as yet. The mechanism of this reaction, based on kinetic experiments, is being reported in this paper

EXPERIMENTAL

<u>Materials</u> - Sulphides were either commercial products or prepared by known methods^{3,8,10} and were purified by either distillation under reduced pressure or recrystallization. The purity was checked by comparing their bp/mp with the literature values. Potassium permanganate of analytical grade was used. Acetic acid (IDPL) was allowed to stand over potassium permanganate for 24 h and then fractionated.

 $\frac{\text{Kinetic Measurements}}{\text{by keeping an excess (x 10 or greater) of the substrate over permanganate. The reactions were carried out at constant temperature (± 0.05 K) in 1:1 (v/v) acetic acid-water, unless stated otherwise. Reactions were followed on a Hi-Tech model SFL-44 stopped-flow spectrometer which was connected to an MCS-1 data processing system. The data were transfered to an Apple IIE PC for analysis and printing. The rate of diappearance of permanganate was monitered at 525 nm. The pseudo-first-order rate constants, <math display="inline">k_1$, were calculated by a computer programme specifically

written for the spectrometer. All rate constants are average of two or more experiments and were reproducible to within \pm 2%. Excess of fluoride ions (0.005 M) was added to prevent reactions of Mn(III)/Mn(IV).¹¹

<u>Product Analysis</u> - MeSPh (0.005 mol) was treated in l:1(v/v) acetic acid-water (10 ml) with permanganate (0.002 mol) and NaF (0.001 mol) at room temperature for 24 h. The solution was

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concentrated, diluted with water and extracted with chloroform $(3 \times 15 \text{ ml})$. The chloroform extract was dired over anhydrous magnesium sulphate, the solvent was removed by evaporation and the residue was analysed by i.r. spectroscopy. The spectrum was identical with that of MePhSO. The peaks characteristic of the sulphide and the sulphone could not be detected. The completely reduced reaction mixtures were colourless, indicating that permanganate has been reduced to Mn(II) (eq. 1).

$$5 \text{ MeSPh} + 2 \text{ MnO}_4^- + 6 \text{ H}^+ \longrightarrow 5 \text{ MeSOPh} + 2 \text{ Mn}^{+2} + 3 \text{ H}_2^0$$
 (1)

RESULTS

The rate data were obtained for all the sulphides studied. Since the results are similar only representative data are reproduced here.

The oxidation of the sulphides by permanganate is of total second order, first order with respect to the each reactant. The pseudo-first-order rate constants at different initial concentrations of the sulphide and permanganate ion are recorded in Table 1.

10 ⁴ [MnO ₄ ⁻], M	[MeSPh], M	[H ⁺], M	k ₁ , s ⁻¹
1.0	0.05	0.01	10.7 ± 0.05
2.0	0.05	0.01	10.6 ± 0.07
4.0	0.05	0.01	10.7 ± 0.10
8.0	0.05	0.01	10.5 ± 0.20
10.0	0.05	0.01	11.0 ± 0.20
4.0	0.01	0.01	2.15 ± 0.03
4.0	0.03	0.01	6.50 ± 0.11
4.0	0.07	0.01	15.0 ± 0.20
4.0	0.15	0.01	32.4 ± 0.31
4.0	0.30	0.01	64.5 ± 0.69
4.0	0.07	0.03	15.4 ± 0.30
4.0	0.07	0.08	15.1 ± 0.27
4.0	0.07	0.10	15.5 ± 0.22
4.0	0.07	0.10^{a}	15.0 ± 0.30
4.0	0.07	0.10 ^D	14.8 ± 0.32
4.0	0.07	0.20	15.4 ± 0.25
^a in AcOD-D ₂ O solvent	, ^b contained 10^{-3} M acrylonitril	e	

Table 1. Rate constants of the oxidation of methyl phenyl sulphide by permanganate ion at 298 K

The plot of 1/[sulphide] against $1/k_1$ is a straight line passing through the origin. Thus a reaction pathway involving the formation of an intermediate complex in a fast preequilibrium and its slow decomposition can be excluded though reactions of this type have been reported earlier in the oxidation of sulphides.⁴ The rate of oxidation of MeSPh is independent of

The rate of oxidation did not change either in deuterated solvents or in the presence of acrylonitrile as a radical scavanger. These results exclude the participation of water in the rate-determining step and the possibility of a radical mechanism.

<u>Solvent Effect</u> - The reaction rate is decreased by increasing the amount of acetic acid in the solvent (Table 2).

Table 2.	Dependence	of	the	rate	of	oxidation	on	solvent	composition ^a
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hydrogen ion concentration (Table 1).

%AcOH(v/v) ^b	25	40	50	60	77.6	87.4	93.3
k ₂ , M ⁻¹ s ⁻¹	505	287	215	138	94.0	53.0	24.2
^a Temperature	298 K,	[MnO ₄ ⁻] 3 x 10 ⁻	⁴ M, [H ⁺] O	.01 M, $k_2 = k$	1/[MeSPh];	^b rest was wa	ater

<u>Substituent Effects</u> - The rates of oxidation of a number of <u>ortho-</u>, <u>meta-</u> and <u>para-</u>substituted phenyl methyl sulphides, alkyl phenyl sulphides, dialkyl sulphides and diphenyl sulphide were determined at different temperatures and the activation parameters were evaluated (table 3).

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Substituent		k ₂ , M ^{−1} s	-1		Δ H [*]	∆ s*
	278 K	288 K	298 K	308 K	kJ mol ⁻¹	$J mol^{-1} K^{-1}$
	· ·		(i) Aryl	methyl sulp	hide	
H p-OMe p-Me p-i-Pr p-F p-C1 p-Br p-COMe p-NO ₂	77.3 253 158 140 59.0 31.3 26.6 9.85 2.77	120 400 244 228 105 59.7 51.8 20.0 6.94	215 592 381 363 163 104 86.0 37.4 14.2	350 845 546 530 263 180 153 71.2 31.5	$\begin{array}{c} 33.5\pm0.6\\ 26.1\pm0.4\\ 27.2\pm0.4\\ 29.3\pm0.4\\ 32.6\pm0.6\\ 38.8\pm0.3\\ 38.5\pm0.7\\ 44.2\pm0.4\\ 54.5\pm1.0 \end{array}$	- 87±2.1 -104±1.3 -104±1.2 - 98±1.5 - 93±2.1 - 76±1.0 - 78±2.6 - 66±1.3 - 39±3.2
<u>p</u> -COOMe <u>p</u> -COOH <u>m</u> -OMe <u>m</u> -Me <u>m</u> -C1 <u>m</u> -NO ₂	11.7 12.2 48.0 108 17.5 3.75	22.5 24.9 83.4 185 34.7 8.20	43.0 46.3 146 284 65.8 18.3	76.2 84.5 244 450 121 36.4	42.1±0.3 43.3±0.3 36.2±0.4 31.0±0.5 43.3±0.2 51.7±0.5	- 72±0.9 - 68±1.0 - 82±1.1 - 93±1.6 - 64±1.3 - 47±1.6
<u>o</u> -Me <u>o</u> -OMe <u>o</u> -F <u>o</u> -C1. <u>o</u> -Br <u>o</u> -NO ₂	45.4 35.0 14.0 8.57 8.02 0.84	80.0 63.5 25.6 17.5 15.5 2.14	134 110 45.0 33.7 29.0 5.10	218 185 75.1 62.6 50.8 11.4	34.7±0.1 37.0±0.8 37.4±0.5 44.6±1.2 41.4±0.7 59.4±0.5	- 88±0.3 - 81±1.1 - 88±0.8 - 66±1.0 - 78±0.9 - 32±0.3
<u>о</u> -СООМе <u>о</u> -СООН	13.1 11.2	27.0 21.8	52.2 40.2	100 70.5	45.6±0.6 41.1±0.7	- 59±0.8 - 76±0.5
			(ii) Alky	l phenyl su	lphides	
Et n-Pr i-Pr t-Bu	100 80.1 89.7 54.1	165 138 142 92.0	274 225 241 130	445 350 400 203	33.0±0.4 32.5±0.3 33.1±0.9 28.2±1.0	- 87±1.4 - 91±0.9 - 88±3.2 -109±3.3
			(iii) Oth	er sulphide	25	
Me ₂ S	175	283	474	741	32.0±0.4	- 86±1.5
Pr ₂ S	341	500	765	1080	25.1±0.4	-105±1.3
Ph ₂ S	9.30	20.3	38.4	78.7	47.6±0.8	- 54±2.6

Table 3. Rate constants and activation parameters of the oxidation of sulphides by permanganate

DISCUSSION

The entropy and enthalpy of activation of the oxidation of all the thirty sulphides are linearly related (r=0.9878). The value of isokinetic temperature evaluated from this plot is $437 \pm 47 \text{ K}$.^{12,13} The correlation was tested and found genuine by applying Exner's criterion.¹⁴ The value of isokinetic temperature calculated from Exner's plot of log k₂ at278 K <u>vs.</u> log k₂ at 308 K (r=0.9960, slope = 0.7577) is 466±12 K. The linear isokinetic relationship suggests that all the sulphides are oxidised by the same mechanism. Current views^{15,16} do not attach much importance to isokinetic temperature, though a linear correlation is usually a necessary condition for the validity of linear free energy relationships.

<u>Solvent Effect</u> - The plot of log k_2 against the inverse of dielectric constant is non-linear. The observed solvent effect (Table 2) lead to the conclusion that the transition state is more polarised than the reactants. An opposite effect is expected for a reaction a neutral species and a negative ion, if the latter was to attack as a nucleophile. Thus it seems that the sulphide suffers an electrophilic attack by a permanganate ion. This results in a positive polarization of the sulphur atom and an increase in the negative charge on the permanganate ion. The increased polarity of the transition state is facilitated by an increase in the ionizing power of the solvent.

The rates of the oxidation at different solvent compositions were analysed in terms of Grunwald-Winstein 17 equation (2).

$$\log k = \log k_0 + mY$$
(2)

The log k₂ versus Y plot was linear (r = 0.9969) with m = 0.39 \pm 0.01 and log k₀ = 1.58 \pm 0.03. The value of m is consistent with S_N² attack by the sulphide-sulphur on a permanganate-oxygen. ¹⁷

<u>Correlation Analysis of Reactivity</u> - Data in table 3 show that the reactivity of different sulphides follows the order of nucleophilicity : $Pr_2S > Me_2S > MeSPh > Ph_2S$

The rates of the oxidation of \underline{m} - and \underline{p} -substituted aryl methyl sulphides correlate well with Hammett constants with negative reaction constants (Table 4). The negative reaction constant

Table 4. Correlation of the rate of the oxidation of \underline{m} - and \underline{p} - substituted aryl methyl sulphides in Hammett's equation

Temp., K	278	288	298	308
P	-1.84±0.01	~1.67±0.03	-1.52±0.02	-1.36±0.03
r	0.9994	0.9990	0.9988	0 9980
SD	0.020	0.024	0.025	0.029

r = Coefficient of correlation, SD = Standard deviation

No. of data points = 15 including that of the unsubstituted compound

points to an electrophilic attack on the sulphur atom by a permanganate ion. The magnitude of the reaction constant is smaller than those observed in the reaction proceeding via halogenosulphonium cations. The values of the reaction constant for the formation of RArSCl⁺ and RArSBr⁺ are -4.25^{1a} and -3.20^{2b} respectively. This suggests that in the transition state of this reaction the electron-deficiency on the sulphur atom is not very high, but is similar to that in the oxidation of sulphides by hydrogen peroxide¹⁸ ($\rho = -1.13$), peroxyhexanoylnitrate⁷ ($\rho = -1.7$) and by per-iodate ion⁸($\rho = -1.40$), where the formation of a sulphurane intermediate has been suggested.

Correlation of the rates of the oxidation of alkyl phenyl sulphides separately with Taft's σ^* and E_s values did not yield satisfactory correlations. The rates were, therefore, analysed in terms of Pavelich-Taft¹⁹ equation (3) of dual substituent-parameters.

$$\log k_2 = \rho^* \mathcal{O}^* + \delta E_s + h \tag{3}$$

The number of compounds (five) is rather small for an analysis by a biparametric equation but the correlations are excellent and the results (Table 5) can be used in a qualitative way.

Table 5. Correlation of the rates of the oxidation of alkyl phenyl sulphides in Pavelich-Taft equation

Temp., K	<u>^*</u>	δ	R	SD	
278	- 1.22	0.35	0.9972	0.011	<u></u>
288	- 1.12	0.33	0.9830	0.025	
298	- 1.27	0.40	0.9977	0.012	
308	- 1.38	0.43	0.9998	0.004	
R = Coefficient o	of multiple correlation	; No. of data poin	ts = 5		

The negative polar reaction constant confirms that the electron-donating power of the alkyl groups enhances the rate. The steric effect plays a relatively minor inhibitory role.

The rates of the oxidation of the <u>ortho</u>-substituted phenyl methyl sulphides did not yield significant correlation with either Taft's polar or steric substituent constants. The rates at 298 K were, therefore, analysed in terms of Charton's ²⁰ equations (4) and (5). In eqs. (4) and (5), $G_{\rm I}$, $G_{\rm R}$ and V represent field, resonance, and steric subsituent constants and the values used were those compiled by Aslem <u>et al.</u> ²¹

$$\log k_{\text{ortho}} = \alpha \sigma_{\text{I}} + \beta \sigma_{\text{R}} + \phi V + h \tag{5}$$

$$\log k_2 = -1.89 \ \mathcal{O}_I = -0.70 \ \mathcal{O}_R + 2.23$$

$$R = 0.9602; \ SD = 0.152; \ n = 9$$
(6)

where n is the number of data points including that of unsubstituted phenyl methyl sulphide.

In multiple linear regression using eq. (4), the coefficient of multiple correlation (R) is poor and the standard deviation is high (eq. 6). The correlation in terms of eq. (5) is also poor if all the <u>ortho-</u> substituted compounds are included (eq. 7). However, the correlation improves substantially if the rate data of <u>ortho-</u>COOMe and <u>ortho-</u>COOM are exluded (eq. 8).

$$\log k_2 = -1.84 \ \mathcal{C}_I - 0.63 \ \mathcal{C}_R - 0.05 \ V + 2.24$$
(7)

$$R = 0.9610; \ SD = 0.165; \ n = 9$$

$$\log k_2 = -1.37 \ \mathcal{C}_I - 0.46 \ \mathcal{C}_R - 0.47 \ V + 2.31$$
(8)

$$R = 0.9991; \ SD = 0.032; \ n = 7$$

The behaviour of ortho-nitro group is consistent with the planar confirmation.

The deviations noted in the case of <u>ortho-COOM</u>e and <u>ortho-COOH</u> substituted sulphides can be attributed to the moderate anchimeric assistance provided by these groups to the reaction by stabilizing the positively polarized sulphur in the transition state. The values of k_2 for the oxidation of <u>ortho-COOM</u>e and <u>ortho-COOH</u> substituted aryl methyl sulphides, calculated by eq. (8) are 13.2 and 14.4 M⁻¹ s⁻¹, whereas the observed values are 52.2 and 40.2 M⁻¹ s⁻¹ respectively. The ratio k_{obs}/k_{calc} is 3.95 and 2.90 for the <u>ortho-COOM</u>e and <u>ortho-COOH</u> substituted compounds respectively. The ratio k_{obs}/k_{calc} represents the rate-enhancement caused by the neighbouring group participation.

The reaction constants and the statistical data for the correlation of the rate of oxidation of <u>ortho</u>-substituted aryl methyl sulphides are recorded in table 6. The contribution of resonance

Temp., K	ø	ß	ø	R	SD	PR	PS
278	- 1.56	- 0,58	- 0.62	0,9998	0.016	27.1	22,5
288	- 1.46	- 0.54	- 0.53	0.9996	0.018	27.0	20.9
298	- 1.37	- 0.46	- 0.47	0.9991	0.032	25.1	20.4
308	- 1.27	- 0.41	- 0.42	0.9977	0.048	24.0	20.0
No. of dat	a points =	7 including <u>ortho</u> -COOH	that of the compounds	e unsubstitute were not cons	d compound; idered	data of <u>orth</u>	o-COOMe and

Table 6. Correlation analysis of the rates of oxidation of <u>ortho</u>-substituted aryl methyl sulphides by Charton's method

effect to the polar effects, P_R , and that of the steric effect to the total effect of the <u>ortho-</u>groups, P_S , were calculated by Charton's method. ²⁰ The results indicate that like alkyl phenyl sulphides, in the oxidation of the <u>ortho-</u>compounds also the field effect is more predominating. Both resonance and steric effects play relatively minor roles.

<u>Mechanism</u> - The experimental results can be accounted for in terms of a mechanism involving a rate-determining electrophilic oxygen transfer from permanganate ion to the sulphide (eq. 9), similar to those suggested for the oxidations of sulphides and iodide ions by periodate ion, ⁸, ²² and the oxidation of sulphides by hydrogen peroxide. ¹⁸ The nuleophilic attack of sulphur on a permanganate-oxygen, involving an oxygen trnsfer, may be viewed as an S_N^2 process. Low magnitudes of the polar reaction constants and moderate degree of anchimeric assistance by the neighbouring groupsalso support a transition state depicted in eq. (9) rather than the formation of a sulphonium ion as shown in eq. (10). Further, the lack of solvent isotope effect and the non-

-dependence of the reaction rate on hydrogen ion concentration exclude the participation of water as a nucleophile and proton-transfer agent in the rate-determining step. The value of the solvent reaction constant (m = 0.39) is also in the range for S_N^2 reactions.¹⁷

The permanganate oxidation of sulphides may involve a cyclic intermediate as has been suggested in many reactions of permanganate ion. 23 However, the cyclic intermediates also













exhibit a sulphurane structure (eq. 11). The cyclic intermediate would be highly strained in view of the apical position of a lone pair or an alkyl group. The steric requirements of the reaction (11) would be higher as compared to those of reaction (9) and the observed small values of steric constants are thus consistent with the proposed acyclic sulphurane mechanism. The formation of a cyclic sulphurane intermediate also entails a more exacting specificity of orientation and should result in a much larger negative entropy of activation than observed. The values of entropy of activation obtained in this reaction is very close to the values obtained in the typical reactions involving oxygen transfer e.g., oxidation of iodide ion by periodate ²² and that of sulphides by hydrogen peroxide ¹⁸ (Δ S^{*} = - 96 and - 115 J mol⁻¹ K⁻¹ respectively).

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