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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 o-COOMe and o-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 acid[6] 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

Materials - 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.

Kinetic Measurements - Kinetic measurements were carried out under pseudo-first-order conditions 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, 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 ± 2 %. Excess of fluoride ions (0.005 M) was added to prevent reactions of Mn(III)/Mn(IV).[11]

Product Analysis - MeSPh (0.005 mol) was treated in 1:1(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 concentrated, diluted with water and extracted with chloroform (3 x 15 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).

$$5\ \mathrm{MeSPh} + 2\ \mathrm{MnO_4^-} + 6\ \mathrm{H^+} \longrightarrow 5\ \mathrm{MeSOPh} + 2\ \mathrm{Mn^{+2}} + 3\ \mathrm{H_2O} \qquad (1)$$

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.

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

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[b]	14.8 ± 0.32
4.0	0.07	0.20	15.4 ± 0.25

[a] in AcOD-D_2O solvent, [b] contained 10^{-3} M acrylonitrile

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 hydrogen ion concentration (Table 1).

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.

Solvent Effect - 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]

%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^-] 3×10^{-4} M, [H^+] 0.01 M, $k_2 = k_1$/[MeSPh]; [b] rest was water

Substituent Effects - The rates of oxidation of a number of ortho-, meta- and para-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).

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

Substituent	k_2, M^{-1} s^{-1}				ΔH^*	ΔS^*
	278 K	288 K	298 K	308 K	kJ mol^{-1}	J mol^{-1} K^{-1}
			(i) Aryl methyl sulphide			
H	77.3	120	215	350	33.5±0.6	- 87±2.1
p-OMe	253	400	592	845	26.1±0.4	-104±1.3
p-Me	158	244	381	546	27.2±0.4	-104±1.2
p-i-Pr	140	228	363	530	29.3±0.4	- 98±1.5
p-F	59.0	105	163	263	32.6±0.6	- 93±2.1
p-Cl	31.3	59.7	104	180	38.8±0.3	- 76±1.0
p-Br	26.6	51.8	86.0	153	38.5±0.7	- 78±2.6
p-COMe	9.85	20.0	37.4	71.2	44.2±0.4	- 66±1.3
p-NO_2	2.77	6.94	14.2	31.5	54.5±1.0	- 39±3.2
p-COOMe	11.7	22.5	43.0	76.2	42.1±0.3	- 72±0.9
p-COOH	12.2	24.9	46.3	84.5	43.3±0.3	- 68±1.0
m-OMe	48.0	83.4	146	244	36.2±0.4	- 82±1.1
m-Me	108	185	284	450	31.0±0.5	- 93±1.6
m-Cl	17.5	34.7	65.8	121	43.3±0.2	- 64±1.3
m-NO_2	3.75	8.20	18.3	36.4	51.7±0.5	- 47±1.6
o-Me	45.4	80.0	134	218	34.7±0.1	- 88±0.3
o-OMe	35.0	63.5	110	185	37.0±0.8	- 81±1.1
o-F	14.0	25.6	45.0	75.1	37.4±0.5	- 88±0.8
o-Cl	8.57	17.5	33.7	62.6	44.6±1.2	- 66±1.0
o-Br	8.02	15.5	29.0	50.8	41.4±0.7	- 78±0.9
o-NO_2	0.84	2.14	5.10	11.4	59.4±0.5	- 32±0.3
o-COOMe	13.1	27.0	52.2	100	45.6±0.6	- 59±0.8
o-COOH	11.2	21.8	40.2	70.5	41.1±0.7	- 76±0.5
			(ii) Alkyl phenyl sulphides			
Et	100	165	274	445	33.0±0.4	- 87±1.4
n-Pr	80.1	138	225	350	32.5±0.3	- 91±0.9
i-Pr	89.7	142	241	400	33.1±0.9	- 88±3.2
t-Bu	54.1	92.0	130	203	28.2±1.0	-109±3.3
			(iii) Other sulphides			
Me_2S	175	283	474	741	32.0±0.4	- 86±1.5
Pr_2S	341	500	765	1080	25.1±0.4	-105±1.3
Ph_2S	9.30	20.3	38.4	78.7	47.6±0.8	- 54±2.6

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 ± 47 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 k_2 at278 K vs. log k_2 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.

Solvent Effect - 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 ofthe oxidation at different solvent compositions were analysed in terms of Grunwald-Winstein [17] equation (2).

$$\log k = \log k_o + m Y \qquad (2)$$

The log k_2 versus Y plot was linear ($r = 0.9969$) with $m = 0.39 \pm 0.01$ and $\log k_o = 1.58 \pm 0.03$. The value of m is consistent with S_N2 attack by the sulphide-sulphur on a permanganate-oxygen.[17]

Correlation Analysis of Reactivity - 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 m- and p-substituted aryl methyl sulphides correlate well with Hammett constants with negative reaction constants (Table 4). The negative reaction constant 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 peroxide[18] ($\rho = -1.13$), peroxyhexanoylnitrate[7] ($\rho = -1.7$) and by periodate ion[8]($\rho = -1.40$), where the formation of a sulphurane intermediate has been suggested.

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

Temp., K	278	288	298	308
ρ	-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

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-Taft[19] equation (3) of dual substituent-parameters.

$$\log k_2 = \rho^* \sigma^* + \delta E_s + h \qquad (3)$$

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	ρ^*	δ	R	SD
278	- 1.22	0.35	0.9972	0.011
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 of multiple correlation; No. of data points = 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 ortho-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), σ_I, σ_R and V represent field, resonance, and steric subsituent constants and the values used were those compiled by Aslem *et al.*[21]

$$\log k_{ortho} = \alpha \sigma_I + \beta \sigma_R + h \qquad (4)$$

$$\log k_{ortho} = \alpha \sigma_I + \beta \sigma_R + \phi V + h \qquad (5)$$

$$\log k_2 = - 1.89 \sigma_I - 0.70 \sigma_R + 2.23 \qquad (6)$$

$R = 0.9602$; $SD = 0.152$; $n = 9$

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 ortho- substituted compounds are included (eq. 7). However, the correlation improves substantially if the rate data of ortho-COOMe and ortho-COOH are exluded (eq. 8).

$$\log k_2 = -1.84\,\sigma_I - 0.63\,\sigma_R - 0.05\,V + 2.24 \qquad (7)$$

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

$$\log k_2 = -1.37\,\sigma_I - 0.46\,\sigma_R - 0.47\,V + 2.31 \qquad (8)$$

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

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

The deviations noted in the case of ortho-COOMe and ortho-COOH 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 ortho-COOMe and ortho-COOH 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 ortho-COOMe and ortho-COOH 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 ortho-substituted aryl methyl sulphides are recorded in table 6. The contribution of resonance effect to the polar effects, P_R, and that of the steric effect to the total effect of the ortho-groups, P_S, were calculated by Charton's method.[20] The results indicate that like alkyl phenyl sulphides, in the oxidation of the ortho-compounds also the field effect is more predominating. Both resonance and steric effects play relatively minor roles.

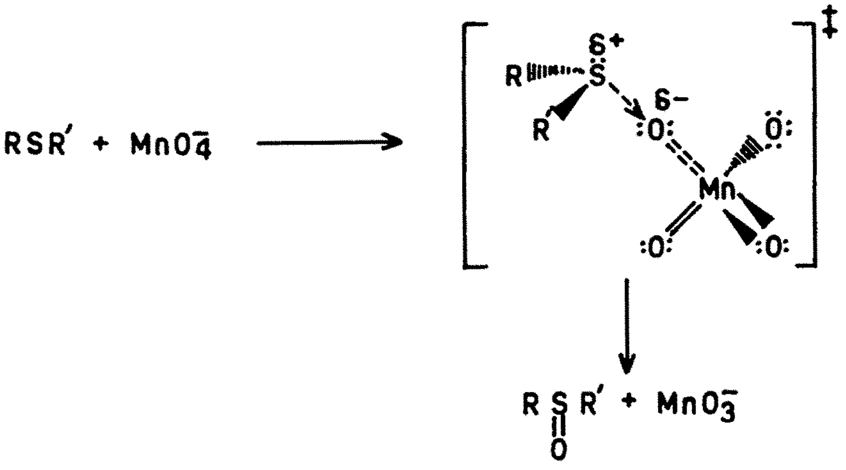
Table 6. Correlation analysis of the rates of oxidation of ortho-substituted aryl methyl sulphides by Charton's method

Temp., K	α	β	ϕ	R	SD	P_R	P_S
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

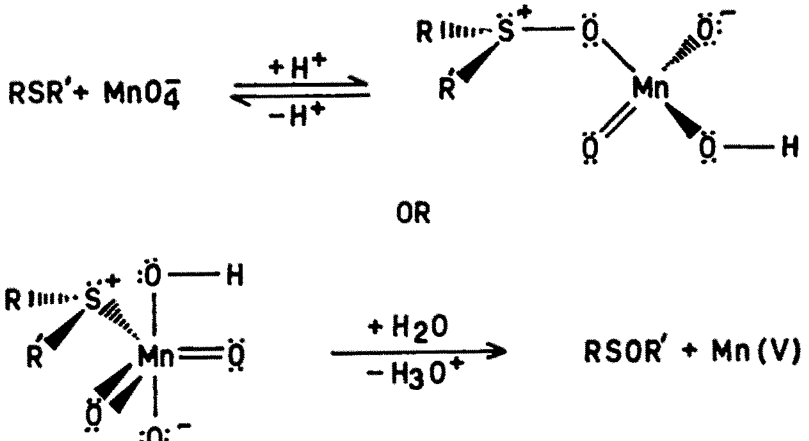
No. of data points = 7 including that of the unsubstituted compound; data of ortho-COOMe and ortho-COOH compounds were not considered

Mechanism - 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_N2 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_N2 reactions.[17]

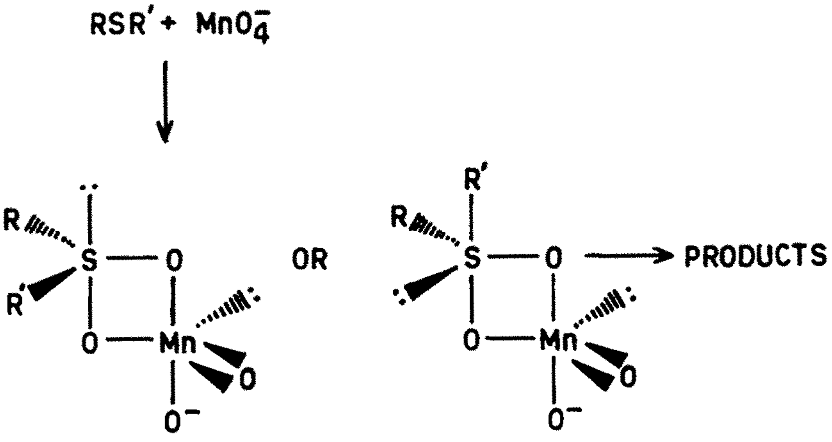
The permanganate oxidation of sulphides may involve a cyclic intermediate as has been suggested in many reactions of permanganate ion.[23] However, the cyclic intermediates also


RSR′ + MnO₄⁻
δ+
δ−
‡
RSR′ (S=O) + MnO₃⁻

(9)


RSR′+ MnO₄⁻
+H⁺
−H⁺
OR
+H₂O
−H₃O⁺
RSOR′ + Mn(V)

(10)


RSR′+ MnO₄⁻
OR
PRODUCTS

(11)

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 obserevd 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] (ΔS^* = - 96 and - 115 J mol^{-1} K^{-1} respectively).

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