Kinetics of the Oxidation of Organic Sulphides by Pyridinium Fluorochromate

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The kinetics of the oxidation of a number of monosubstituted aryl methyl, alkyl phenyl, dialkyl, and diphenyl sulphides by pyridinium fluorochromate (PFC) to yield the corresponding sulphoxides have been studied. The reaction is first order with respect to the sulphide and PFC. The reaction exhibited negative polar reaction constants and a small degree of steric hindrance. The analysis of the rates in 19 different solvents indicated an electrophilic attack of a PFC oxygen on the sulphide yielding a polar transition state. Moderate anchimeric assistance was observed in the oxidation of *o*-CO_2H- and *o*-CO_2Me-substituted phenyl methyl sulphides. A mechanism involving a one-step electrophilic oxygen transfer from PFC to the sulphide and a polar transition state has been proposed.

Pyridinium fluorochromate (PFC) has been described[1] as a more powerful and versatile oxidant than pyridinium chlorochromate (PCC).[2] The available reports indicate that oxidations of alcohols by PFC[3] and PCC[4] present different kinetic pictures. The kinetics of the oxidation of three sulphides by PCC were reported earlier.[5] In continuation of our work on the oxidations by PCC and PFC,[3,4] we now report the kinetics of the oxidation of a series of *o*-, *m*-, and *p*-substituted phenyl methyl sulphides, alkyl phenyl sulphides, dialkyl sulphides, and diphenyl sulphide by PFC. The mechanistic aspects are discussed.

Experimental

Materials.—The sulphides were either commercial products or prepared by known methods,[6-8] and were purified by distillation under reduced pressure or recrystallization. Their purity was checked by comparing their b.p.s or m.p.s with the literature values. PFC was prepared by the reported method.[1] Solvents were purified by the usual methods.[9]

Product Analysis.—Methyl phenyl sulphide (0.006 mol) and PFC (0.004 mol) were dissolved in dimethylformamide (DMF) (20 ml) and the mixture was allowed to stand for 24 h. Most of the solvent was removed under reduced pressure. The residue was diluted with water and was extracted with chloroform (3 × 50 ml). The chloroform extract was dried ($MgSO_4$), the solvent was removed by evaporation, and the residue was analysed by i.r. spectroscopy. The spectrum was identical with that of MeSOPh. Peaks characteristic of MeSPh and $MeSO_2Ph$ could not be detected.

Kinetic Measurements.—Kinetic measurements were carried out under pseudo-first-order conditions by keeping an excess (× 15 or greater) of the substrate over PFC. The reactions were carried out at constant temperature (± 0.05 K). The solvent was DMF, unless stated otherwise. The reactions were followed by monitoring the decrease in the concentration of PFC at 356 nm. Reactions, too fast to be measured by the conventional techniques, were followed on a Hi-Tech model SFL-44 stopped-flow spectrophotometer system. The pseudo-first-order rate constant, k_1, was evaluated from the linear plots of log [PFC] against time. The second-order rate constant, k_2, was obtained from the relation $k_2 = k_1/[\text{sulphide}]$.

Table 1. Rate constants for the oxidation of methyl phenyl sulphide by PFC at 298 K

10^4 [PFC]/M	[MeSPh]/M	$10^2\,k_1/s^{-1}$
2.0	0.05	3.60 ± 0.04
4.0	0.05	3.72 ± 0.03
6.0	0.05	3.56 ± 0.03
8.0	0.05	3.63 ± 0.02
10.0	0.05	3.70 ± 0.04
15.0	0.05	3.65 ± 0.05
20.0	0.05	3.60 ± 0.03
5.0	0.10	7.30 ± 0.05
5.0	0.20	14.4 ± 0.10
5.0	0.30	22.0 ± 0.12
5.0	0.40	29.2 ± 0.17
5.0	0.50	36.7 ± 0.15
5.0	0.75	54.6 ± 0.15
5.0	0.75[a]	54.8 ± 0.20

[a] Contained 10^{-3}M-acrylonitrile.

Table 2. Rate constants for the oxidation of methyl phenyl sulphides by PFC in different solvents at 298 K

Solvent	$10^3\,k_2/l\ mol^{-1}\ s^{-1}$
DMF	730
Chloroform	527
Carbon disulphide	40.1
1,2-Dichloroethane	444
Dichloromethane	565
Dimethyl sulphoxide	1 630
Acetone	314
Butanone	250
Nitrobenzene	636
Benzene	318
Cyclohexane	10.0
Toluene	79.3
Acetophenone	485
Tetrahydrofuran	186
t-Butyl alcohol	223
Dioxane	200
1,2-Dimethoxyethane	147
Acetic acid	253
Ethyl acetate	130

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

	$10^3\ k_2$/l mol^{-1} s^{-1}					
Substituent	278 K	288 K	298 K	308 K	ΔH^*/kJ mol^{-1}	$-\Delta S^*$/J mol^{-1} K^{-1}
(i) Aryl methyl sulphides						
H	170	378	730	1 400	47.2 ± 0.6	89 ± 2.0
p-OMe	592	1 080	2 130	3 700	41.4 ± 0.8	99 ± 2.6
p-Me	353	840	1 310	2 530	42.6 ± 2.3	98 ± 7.9
p-Pr^i	344	706	1 270	2 240	41.7 ± 0.6	103 ± 2.1
p-F	133	304	590	1 130	47.9 ± 0.8	88 ± 2.6
p-Cl	64.4	137	315	622	51.8 ± 0.8	80 ± 2.8
p-Br	62.0	150	291	654	52.5 ± 1.2	78 ± 4.2
p-COMe	15.2	48.3	103	225	60.6 ± 2.4	60 ± 8.1
p-NO_2	4.30	13.0	36.5	97.2	71.4 ± 0.2	32 ± 0.4
p-CO_2Me	25.4	64.8	144	315	57.0 ± 0.5	69 ± 1.7
p-CO_2H	20.6	54.3	127	285	59.7 ± 0.4	62 ± 1.4
m-OMe	98.4	220	483	1 000	52.6 ± 0.3	74 ± 1.0
m-Me	244	540	815	1 770	43.6 ± 1.4	99 ± 4.7
m-Cl	28.0	76.5	179	383	59.5 ± 1.0	60 ± 3.3
m-NO_2	5.82	22.8	52.6	130	69.9 ± 1.1	34 ± 3.7
o-Me	96.2	228	466	845	49.1 ± 1.3	87 ± 4.3
o-OMe	74.0	183	341	703	50.0 ± 1.4	85 ± 4.5
o-F	34.2	69.1	152	303	49.6 ± 0.9	94 ± 3.1
o-Cl	17.1	40.6	90.5	212	56.9 ± 0.8	73 ± 2.9
o-Br	14.8	36.0	75.0	177	55.7 ± 1.1	79 ± 3.8
o-NO_2	1.60	3.83	8.00	22.8	59.3 ± 2.6	84 ± 9.1
o-CO_2Me	91.2	218	480	884	51.7 ± 1.2	78 ± 4.2
o-CO_2H	127	260	530	1 110	48.8 ± 0.9	86 ± 3.1
(ii) Alkyl phenyl sulphides						
Et	234	500	1 000	1 780	45.8 ± 0.7	91 ± 2.4
Pr^n	184	414	837	1 590	48.6 ± 0.6	83 ± 1.9
Pr^i	225	469	886	1 730	45.6 ± 0.5	92 ± 1.6
Bu^t	122	263	580	1 020	48.5 ± 1.2	87 ± 4.0
(iii) Other sulphides						
Me_2S	350	737	1 130	2 170	39.5 ± 1.8	110 ± 6.2
Pr_2S	685	1 420	2 530	3 990	39.3 ± 1.9	105 ± 5.0
Ph_2S	23.4	44.5	108	195	49.1 ± 1.9	99 ± 6.4

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 PFC is a second-order process, first order with respect to each reactant. The pseudo-first-order rate constants at different initial concentrations of the sulphide and PFC are recorded in Table 1. The plot of 1/[sulphide] *versus* $1/k_1$ is a straight line, passing through the origin. Thus a reaction pathway involving formation of a complex in a fast pre-equilibrium and its slow decomposition is unlikely, though the formation of a complex in low concentration cannot be excluded. Reactions involving Michaelis–Menten-type kinetics have been reported in the oxidation of sulphides and also in the oxidations by PFC.[3,5] The rate of oxidation did not change in the presence of acrylonitrile as a radical scavanger. Thus the operation of a one-electron oxidation giving rise to free radicals is unlikely.

Solvent Effect.—The rates of oxidation of MeSPh were determined in 19 solvents. The choice of solvents was limited by the solubility of PFC and its reaction with primary and secondary alcohols. The kinetics were similar in all solvents (Table 2).

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 various temperatures and the activation parameters were evaluated (Table 3).

Discussion

The entropy and enthalpy of activation of the oxidation of the 30 sulphides are linearly related (*r* 0.9863). The isokinetic temperature, evaluated from this plot, is 468 ± 40 K.[10,11] The correlation was tested and found genuine by Exner's criterion.[12] The isokinetic temperature calculated from the Exner's plot of $\log k_2$ at 278 K *versus* $\log k_2$ at 308 K (*r* 0.9922, slope 0.7646 ± 0.02), is 478 ± 21 K. The linear isokinetic correlation suggests that all the sulphides are oxidized by the same mechanism.

Solvent Effect.—The rates in 17 solvents (CS_2 and acetic acid were not considered as the complete range of the solvent parameters were not available) were correlated in terms of linear solvation energy relationship (l.s.e.r.) of Kamlet and Taft.[13] The analyses in terms of the triparametric l.s.e.r., a biparametric equation involving π^* and β, and separately with π^* and β did not yield significant correlations.

Analysis in terms of Swain's equation[14] of cation- and anion-solvating concepts [equation (1)] leads to a satisfactory correlation (2).

Table 4. Correlation of the rates of the oxidation of *meta*- and *para*-substituted aryl methyl sulphides in the Hammett equation

T/K	278	288	298	308
ρ	-2.04 ± 0.03	-1.81 ± 0.03	-1.65 ± 0.02	-1.50 ± 0.02
r	0.9987	0.9982	0.9992	0.9988
S.D.	0.035	0.036	0.027	0.024

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

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

T/K	ρ^*	δ	R	S.D.
278	-1.70	0.43	0.9991	0.007
288	-1.45	0.40	0.9982	0.009
298	-1.38	0.35	0.9855	0.022
308	-1.31	0.35	0.9915	0.018

R = Coefficient of multiple correlation; no. of data points = 5.

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

T/K	α	β	φ	R	S.D.	P_S	P_R
278	-1.53	-0.59	-0.69	0.9992	0.04	27.8	24.6
288	-1.62	-0.65	-0.61	0.9998	0.02	28.6	21.2
298	-1.51	-0.48	-0.72	0.9999	0.01	24.1	26.2
308	-1.38	-0.53	-0.58	0.9997	0.02	27.7	23.3

No. of data points = 7, including that of the unsubstituted compound; data of o-CO$_2$Me- and o-CO$_2$H-substituted compounds were excluded.

$$\log k_2 = aA + bB + c \qquad (1)$$

$$\log k_2 = 1.36\,A + 1.68\,B - 2.08 \qquad (2)$$
$$R = 0.9744;\ \text{S.D.} = 0.12;\ n = 19$$

The results show that both the cation- and anion-solvating powers of the solvent play an important role, though cation-solvating power is somewhat more dominant. According to Swain,[14] $(A + B)$ represents the polarity of the solvent. The rates yielded a satisfactory correlation (3) with $(A + B)$ also.

$$\log k_2 = 1.57 \pm 0.10\,(A + B) - 2.07 \qquad (3)$$
$$r = 0.9689;\ \text{S.D.} = 0.13;\ n = 19$$

However, the correlations individually with A and B were poor (r 0.4301 and 0.8248 respectively).

The solvent effect leads to the conclusion that the transition state is more polarized than the reactants. Thus it seems that the sulphide suffers an electrophilic attack by a PFC oxygen atom. This results in positive polarization of the sulphur atom and a negative polarization of the oxygen. The increased polarity of the transition state is facilitated by an increase in the ionizing power of the solvent.

Correlation of Reactivity.—Data in Table 3 show that the reactivity of different sulphides follows the order of their nucleophilicity: Pr$_2$S > Me$_2$S > MeSPh > Ph$_2$S.

The rates of oxidation of *meta*- and *para*-substituted aryl methyl sulphides correlate well with Hammett substituent constants yielding negative reaction constants (Table 4). The negative reaction constant points to an electrophilic attack on the sulphur atom by PFC. The magnitude of the reaction constant is smaller than those observed in the oxidation proceeding *via* halogenosulphonium cations. The values of ρ for the formation of RArSCl$^+$ and RArSBr$^+$ are -4.25 and -3.20 respectively.[15,16] 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 observed in the oxidation of sulphides by hydrogen peroxide[17] (ρ -1.13), peroxyhexanoyl nitrate[18] (ρ -1.7), and periodate ion[7] (ρ -1.40), where the formation of a sulphurane intermediate has been suggested.

Analysis of the rates of oxidation of alkyl phenyl sulphides separately with Taft's σ^* and E_s values did not yield satisfactory correlations. The rates, therefore, were analysed in terms of the Pavelich–Taft[19] equation (4) for dual substituent parameters.

$$\log k_2 = \rho^*\sigma^* + \delta E_s + h \qquad (4)$$

The number of compounds (five) is rather small for an analysis by a biparametric equation but the correlations are excellent (Table 5) and the results can be used in a qualitative way. The negative polar reaction constant confirms that the electron-donating power of the alkyl groups enhances the rate. The steric effect plays a minor inhibitory role.

The rates of oxidation of the *ortho*-substituted aryl methyl sulphides did not yield a 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 (5) and (6). In equations (5) and (6), σ_I, σ_R, and V represent field, resonance, and steric substituent constants respectively; the values used were those compiled by Aslem *et al.*[21]

$$\log k_o = \alpha\sigma_I + \beta\sigma_R + h \qquad (5)$$

$$\log k_o = \alpha\sigma_I + \beta\sigma_R + \varphi V + h \qquad (6)$$

$$\log k_2 = -2.25\,\sigma_I - 0.50\,\sigma_R - 0.09 \qquad (7)$$
$$R = 0.8650;\ \text{S.D.} = 0.35;\ n = 9$$

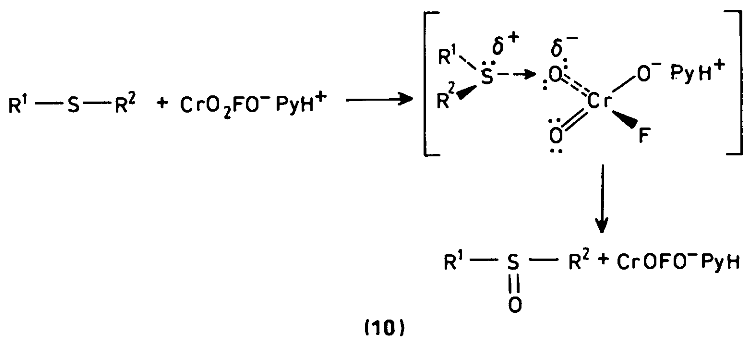
In multiple linear regression using equation (5), the coefficient of multiple correlation (R) is poor and the standard deviation (S.D.) is high [equation (7)]. The correlation in terms of equation (6) is also poor, if all the *ortho*-compounds are included [equation (8)]. However, the correlation improves substantially if the rate data of o-CO$_2$Me and o-CO$_2$H compounds are excluded [equation (9)].

$$\log k_2 = -2.57\,\sigma_I - 1.00\,\sigma_R - 0.32\,V - 0.28 \qquad (8)$$
$$R = 0.8815;\ \text{S.D.} = 0.36;\ n = 9$$

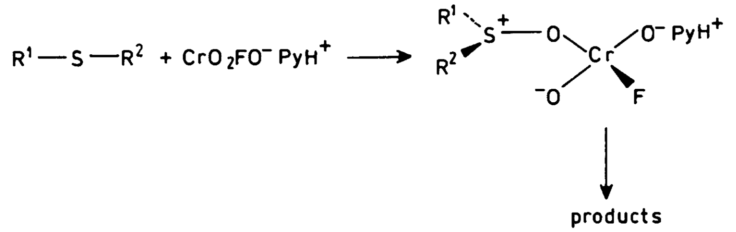
$$\log k_2 = -1.51\,\sigma_I - 0.48\,\sigma_R - 0.72\,\text{V} - 0.04 \qquad (9)$$
$$R = 0.9999;\ \text{S.D.} = 0.012;\ n = 7$$

The behaviour of o-NO$_2$ group is consistent with the planar conformation. The deviations noted in the cases of the o-CO$_2$Me- and o-CO$_2$H-substituted compounds 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 the o-CO$_2$Me- and o-CO$_2$H-substituted sulphides, calculated by equation (9), are 2.29×10^{-2} and 2.69×10^{-2} l mol^{-1} s^{-1} respectively, whereas the observed values are 53.0×10^{-2} and 73.0×10^{-2} l mol^{-1} s^{-1}. The ratio $k_{\text{obs}}/k_{\text{calc}}$ is 21.0 and 19.7 for the o-CO$_2$Me- and o-CO$_2$H-substituted sulphides, respectively. This ratio represents the rate enhancement caused by neighbouring group participation.

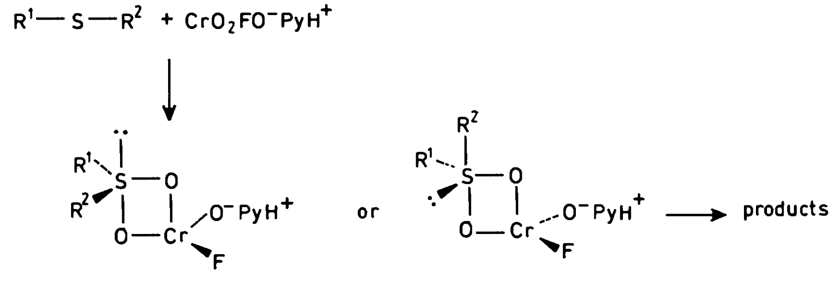
The reaction constants and the statistical data for the *ortho*-substituted aryl methyl sulphides are recorded in Table 6. The contribution of the resonance effect to the polar effects, P_R, and that of steric effect to the total effect of the *ortho*-groups, P_S, were calculated by Charton's method.[20] The results indicate



(10)



(11)



(12)

that as in the case of alkyl phenyl sulphides, in the oxidation of *ortho*-compounds also the field effect is predominating. Both resonance and steric effects play relatively minor roles.

Mechanism.—The experimental results can be accounted for in terms of a mechanism involving rate-determining electrophilic oxygen transfer from PFC to the sulphide [equation (10)], similar to those suggested for the oxidation of sulphides and iodide ions by periodide ion,[7,22] and for the oxidation of sulphides by hydrogen peroxide.[17] The nucleophilic attack of a sulphide sulphur on a PFC oxygen may be viewed as an S_N2 process. Low magnitudes of the polar reaction constants and the moderate degree of anchimeric assistance by the neighbouring groups also support a transition state depicted in equation (10), rather than a sulphonium ion as shown in equation (11). The solvent effect also supports an S_N2-like transition state.

The oxidation of sulphides by PFC may involve a cyclic intermediate as has been suggested in many reactions of Cr^{VI}.[23] However, the cyclic intermediates may also exhibit a sulphurane structure, equation (12). The cyclic intermediate would be highly strained in view of the apical position of a lone pair of electrons or an alkyl group. The steric requirements of the reaction (12) would be higher than those of reaction (10) and the observed small values of steric reaction constant 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 value of the entropy of activation obtained in this reaction is close to the values observed in typical reactions involving oxygen transfer *e.g.*, oxidation of iodide ion by periodate[22] and that of MeSPh by hydrogen peroxide[17] and periodate[7] (ΔS^* −96, −115, and −113 J mol^{-1} K^{-1}, respectively).

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