Kinetics and Mechanism of Oxidation of Organic Sulphides by Lead Tetraacetate

Kalyan K. Banerji
Department of Chemistry, University of Jodhpur, Jodhpur 342 001, India

Kinetics of oxidation of thirty-three organic sulphides, comprising monosubstituted aryl methyl sulphides and alkyl phenyl sulphides, by lead tetraacetate (LTA), to yield the corresponding sulphoxides, have been studied. The reaction is first order with respect to both sulphide and LTA and is catalysed by hydrogen ions. The observed solvent effect ($m = 0.90$ for MeSPh) is explained by a nucleophilic attack of the sulphide sulphur on LTA yielding a polar transition state. The rates of oxidation of *meta*- and *para*-substituted phenyl methyl sulphides were correlated with Taft's and Swain's dual substituent parameter equations. For the *para*-compounds, the best correlation is obtained with σ_I and σ_R^+; the *meta*-substituted compounds correlate best with σ_I and σ_R^0 values. The reaction constants are negative. The oxidation rates of *ortho*-substituted compounds yield an excellent correlation with a triparametric equation involving Taft's σ_I and σ_R^+ parameters, and Charton's steric parameter V. The oxidation of alkyl phenyl sulphides is susceptible to both polar and steric effects of the alkyl groups. A mechanism involving formation of a sulphonium cation, in the rate-determining step, has been proposed.

Kinetics and mechanism of the oxidation of organic sulphides have received considerable attention in recent years. The mechanism depends largely on the nature of the oxidant. Halogenating agents convert sulphides into halogenosulphonium cations.[1-3] The oxidations by peroxo anions,[4] pyridinium chlorochromate,[5] phenyl iodosodiacetate[6] and chromic acid[7] are proposed to involve intermediates with a sulphonium centre. Mechanisms involving sulphurane intermediates have been suggested in oxidations by peroxyhexanoyl nitrate,[8] periodate ion,[8] permanganate[10] and pyridinium fluorochromate.[11] Lead tetraacetate (LTA) is a versatile and strong oxidant. A preliminary study on the kinetics of oxidation of aryl methyl sulphides by LTA has been reported,[12] though a number of synthetic studies involving sulphides and LTA are available.[13] In this paper, kinetics of oxidation of thirty-three organic sulphides by LTA are reported. Attempts have been made to correlate rate and structure.

Experimental

Materials.—The sulphides were either commercial products or prepared by known methods,[3] and were purified by distillation under reduced pressure or crystallization. Their purity was checked by comparing their b.p.s or m.p.s with the literature values. LTA was prepared by the reported method[14] and was purified by recrystallization from glacial acetic acid. Acetic acid was refluxed over chromic oxide for 6 h and then fractionated.

Product Analysis.—Methyl phenyl sulphide (0.01 mol) and LTA (0.01 mol) were dissolved in acetic acid (100 cm^3) and the mixture was allowed to stand for 24 h. Most of the solvent was removed by distillation under reduced pressure and the remaining acetic acid was neutralized with a concentrated solution of sodium carbonate. The resulting mixture was extracted with chloroform (3 × 50 cm^3). The chloroform extract was dried over anhydrous magnesium sulphate, the solvent was removed by evaporation, and the residue was analysed by IR spectroscopy. The spectrum was identical with that of MeSOPh. Peaks characteristic of MeSPh and MeSO$_2$Ph could not be detected.

Kinetic Measurements.—Pseudo-first-order conditions were attained by keeping a large excess (× 20 or greater) of sulphide over LTA. The solvent was glacial acetic acid, unless otherwise stated. The reaction vessels were blackened from outside to prevent any possible photochemical reactions. The reaction was followed by determining unreacted LTA concentration at different time intervals by an iodometric method.[15] The pseudo-first-order rate constant, k_1, was evaluated from the linear plots of log [LTA] *vs.* time by the least squares method. The second-order rate constant, k_2, was obtained from the relation $k_2 = k_1/[\text{sulphide}]$. Duplicate kinetic runs showed that the rate constants were reproducible to within ±4%.

Results

The oxidation of organic sulphides by LTA results in the formation of the corresponding sulphoxides [eqn. (1)].

$$\text{R-S-R}' + \text{Pb(OAc)}_4 \longrightarrow \text{R} - \text{SO} - \text{R}' + \text{Pb(OAc)}_2 + \text{Ac}_2\text{O} \quad (1)$$

Rate Laws.—The oxidation of sulphides by LTA is first order with respect to LTA. Further, the pseudo-first-order rate constants, k_1, do not depend on the initial concentration of LTA. The variation in the concentration of the sulphide indicates that the reaction is first order with respect to the sulphide also. To study the effect of acidity on the reaction rate, the rates were measured in the presence of varying amounts of *p*-toluenesulphonic acid (TsOH). Hydrogen ions catalyse the reaction. Addition of sodium acetate and acrylonitrile did not affect the rate (Table 1).

Effect of Solvent Composition.—The oxidation of methyl phenyl sulphide was studied in solvents containing different proportions of acetic acid and water. The rate of oxidation increases as the amount of water in the solvent is increased (Table 2).

Effect of Substituents.—The rates of oxidation of a number of *ortho*-, *meta*- and *para*-substituted phenyl methyl sulphides and alkyl phenyl sulphides were determined at different temperatures and the activation parameters were calculated (Table 3).

Table 1 Rate constants for the oxidation of methyl phenyl sulphide by LTA at 308 K

[MeSPh]/ mol dm^{-3}	[LTA]/ 10^{-3} mol dm^{-3}	[TsOH]/ mol dm^{-3}	$k_1/10^{-5}$ s^{-1}
1.0	2.5	0.0	8.93
1.0	5.0	0.0	8.70
1.0	8.0	0.0	8.80
1.0	12.0	0.0	8.42
1.0	16.0	0.0	8.53
1.0	20.0	0.0	8.67
0.2	5.0	0.0	1.75
0.4	5.0	0.0	3.50
0.8	5.0	0.0	6.90
1.2	5.0	0.0	10.4
1.6	5.0	0.0	14.0
2.0	5.0	0.0	17.7
0.8	5.0	0.0	8.83[a]
0.8	5.0	0.0	8.75[b]
0.8	5.0	0.1	12.6
0.8	5.0	0.2	18.0
0.8	5.0	0.3	24.4
0.8	5.0	0.5	35.2
0.8	5.0	0.8	52.0

[a] Contained 10^{-2} mol dm^{-3} acrylonitrile. [b] Contained 0.5 mol dm^{-3} sodium acetate.

Table 2 Effect of solvent composition on the oxidation rate[a]

Percentage acetic acid (v/v)	$k_2/10^{-7}$ dm^3 mol^{-1} s^{-1}
100	3.55
99	5.05
96	15.5
93	42.3
86	148
71	770
60	2400

[a] [MeSPh] 1.0 mol dm^{-3}, [LTA] 0.005 mol dm^{-3}, T 298 K

Discussion

A linear isokinetic relationship was observed between log k_2 at 288 K and log k_2 at 318 K (slope 0.8359 ± 0.0151, R 0.9977) for the oxidation of thirty-three sulphides. This suggests that all the sulphides are oxidized by the same mechanism.[16] Further, a linear isokinetic relationship is a necessary condition for the validity of linear free energy relationships.[17] The value of the isokinetic temperature is 690 ± 63 K.

The hydrogen ion dependence has the form: $k_1 = a + b[\mathrm{H}^+]$. This indicates the formation of a protonated species which is more reactive than the unprotonated one. It is proposed that in the presence of TsOH, LTA is protonated to give a stronger oxidant and electrophile [eqn. (2)]. Both LTA and $Pb(OAc)_3^+$ act as reactive oxidizing species. The formation of $Pb(OAc)_3^+$ as a reactive oxidizing species has been suggested previously.[12,13b,c]

$$Pb(OAc)_4 + H^+ \rightleftharpoons Pb(OAc)_3^+ + AcOH \qquad (2)$$

Solvent Effect.—The plot of log k_2 *vs.* the inverse of the permittivity of the solvent is non-linear. The observed solvent effect (Table 2) leads to the conclusion that the transition state is more polarized than the reactants. Thus it seems that LTA undergoes a nucleophilic attack by the sulphide sulphur. This results in a positive polarization of the sulphur atom and a negative polarization of LTA. The increased polarity of the transition state is facilitated by an increase in the ionizing power of the solvent. The solvent effect on the reaction rate was analysed in terms of the Grunwald–Winstein[18] equation [eqn. (3)].

$$\log k_2 = \log k_0 + m\,Y \qquad (3)$$

The log k_2 *vs.* Y plot was linear (R 0.9995) with $m = 0.90 \pm 0.02$ and $\log k_0 = -5.00 \pm 0.15$. The value of m is consistent with an S_N1-type transition state in the oxidation of sulphides by LTA.

Correlation Analysis of Reactivity.—The oxidation rates of *meta-* and *para*-substituted phenyl methyl sulphides failed to show satisfactory correlation with any single substituent-parameter equation. The rates of the *meta-* and *para*-compounds were, therefore, subjected to analysis in terms of Taft's[19] and Swain's[20] dual substituent-parameter (DSP) equations. The rates of the *para*-substituted sulphides show an excellent correlation with σ_I and σ_R^+ values (Table 4). We have used standard deviation (SD), coefficient of multiple correlation (R), and the parameter f as the measures of goodness of fit. f has been defined[21] as SD/root mean square of data points (here log k/k_0). Comparison showed that f is smaller for the σ_R^+ scale than for the other scales by factors of *ca.* 8–50. Thus it is apparent that the rates of oxidation of *para*-substituted phenyl methyl sulphides by LTA correlate best with σ_I and σ_R^+.

The rates of oxidation of the *meta*-compounds show excellent correlation with σ_I and σ_R^0, though the discriminating factor for the precision of fit with the other σ_R scales or with Swain's equation is not as sharp as in the case of *para*-substituted compounds. In fact the correlation with σ_R^- meets the requirements for a satisfactory fit ($f < 0.1$). This agrees with the observation of Ehrenson, Brownlee and Taft[20] that the correlation of *meta*-substituted compounds is generally best with σ_R^0 and that *meta*-substituted compounds are less discriminating.

The reaction constants and statistical data at different temperatures are recorded in Table 5. The value of λ^p (1.15–1.52) showed that the oxidation of the *para*-substituted sulphides is more susceptible to the resonance effect than to the field effect. In the oxidation of the *meta*-compounds, however, the value of λ^m is *ca.* 0.65, indicating the greater importance of the field effect. The magnitude of the reaction constants decreases at higher temperature indicating a decrease in the selectivity. In the case of *para*-compounds, the decrease is more pronounced in the field effect, resulting in a gradual increase in the value of λ^p. In the oxidation of *meta*-compounds, the decrease is of the same order in both the effects, resulting in an almost constant value of λ^m.

In none of the earlier reports on the oxidation of sulphides have DSP equations been used for correlating the effect of structure on reactivity. In oxidations by reagents which involve a direct oxygen transfer *via* an electrophilic attack on the sulphide sulphur, the reaction constants are negative but are of relatively small magnitude, *e.g.* hydrogen peroxide (−1.13),[22] periodate (−1.40),[9] permanganate (−1.52)[10] and peroxydisulphate (−0.56).[4] The reactions involving formation of halogenosulphonium cations, on the other hand, exhibit large negative reaction constants (*cf.* −4.25, −3.2 and −3.75 for the oxidation of sulphides by chloramine-T,[1a] bromine[2b] and NBA[2c] respectively). In the present study, the total effect of the *meta-* and *para*-substituents have been dissected into contributions by inductive and resonance effects. The reaction constants are large and negative. Thus the formation of a strongly electron-deficient sulphur centre in the transition state is indicated.

The rates of oxidation of *ortho*-substituted phenyl methyl sulphides failed to yield any significant correlation with either Taft's polar or steric substituent constants.[23] The rates were, therefore, analysed by Charton's method.[24] The rates were analysed using eqns. (3) and (4), where σ_I, σ_R and

Table 3 Rate constants at different temperatures, and activation parameters of the oxidation of sulphides by LTA

Substituent	$k_2/10^{-7}$ dm^3 mol^{-1} s^{-1} 288 K	298 K	308 K	318 K	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J mol^{-1} K^{-1}
(*i*) Aryl methyl sulphides						
H	138	355	870	2 020	65.7 ± 0.1	−111 ± 0.5
p-Me	600	1 410	3 180	6 820	57.0 ± 0.9	−128 ± 3.1
p-OMe	5 050	15 700	34 500	76 000	65.2 ± 1.2	−80 ± 7.2
p-F	271	801	2 200	5 720	74.8 ± 0.5	−73 ± 0.2
p-Cl	103	310	875	2 330	76.6 ± 0.3	−75 ± 1.0
p-Br	100	294	635	1 740	66.6 ± 1.6	−109 ± 5.1
p-NO_2	6.21	17.7	48.0	123	73.3 ± 0.2	−110 ± 0.6
p-COMe	24.2	64.5	160	395	68.2 ± 0.4	−116 ± 0.3
p-COOMe	19.2	54.8	147	383	73.3 ± 0.4	−100 ± 1.3
p-NH_2	127 000	400 000	834 000	1 770 000	63.4 ± 2.7	−61 ± 9.0
m-Me	256	645	1 550	3 300	62.6 ± 0.5	−116 ± 1.7
m-OMe	134	340	817	1 790	63.4 ± 0.4	−118 ± 1.2
m-NH_2	283	666	1 630	3 530	61.9 ± 0.6	−117 ± 2.1
m-Cl	21.5	63.5	166	405	71.9 ± 0.5	−104 ± 1.7
m-Br	26.4	71.2	178	460	69.7 ± 0.8	−110 ± 2.6
m-I	28.0	74.5	192	440	67.6 ± 0.4	−117 ± 1.4
m-NO_2	1.65	5.34	16.0	46.1	81.9 ± 0.2	−91 ± 0.6
m-CO_2Me	24.3	50.0	132	326	64.0 ± 2.6	−131 ± 8.0
m-COMe	17.0	48.2	124	319	71.6 ± 0.3	−107 ± 0.8
m-F	22.5	64.8	171	414	71.4 ± 0.4	−105 ± 1.2
o-Me	187	483	1 220	2 830	66.6 ± 2.9	−109 ± 2.5
o-OMe	960	2 330	5 270	11 800	60.1 ± 0.3	−110 ± 1.1
o-NO_2	2.25	6.94	20.6	53.5	78.2 ± 0.4	−101 ± 1.2
o-COOMe	7.80	22.5	61.2	160	74.1 ± 0.3	−105 ± 0.8
o-NH_2	32 600	76 000	166 000	340 000	57.0 ± 0.2	−95 ± 0.7
o-Cl	26.2	74.0	192	467	70.6 ± 0.7	−107 ± 1.0
o-Br	19.6	44.5	121	297	67.1 ± 1.9	−122 ± 6.2
o-I	17.7	49.8	132	330	71.7 ± 0.5	−106 ± 1.1
o-CN	4.70	14.2	38.3	100	74.9 ± 0.4	−106 ± 1.2
(*ii*) Alkyl phenyl sulphides						
Et	203	516	1 320	3 040	66.4 ± 0.5	−104 ± 1.7
Pr	150	396	1 000	2 360	67.5 ± 0.2	−103 ± 0.7
Pr^i	187	480	1 140	2 810	65.9 ± 0.7	−107 ± 2.3
Bu^t	70.2	186	477	1 150	68.5 ± 0.3	−106 ± 0.9

Table 4 Correlation of the rates of oxidation of *para*- and *meta*-substituted phenyl methyl sulphides by LTA at 298 K[a]

Substituent constants	ρ_I	ρ_R	*R*	SD	*f*
para-substituted					
$\sigma_I, \sigma_R{}^0$	−2.15	−4.34	0.9427	0.48	0.50
$\sigma_I, \sigma_R{}^{BA}$	−1.95	−3.32	0.9853	0.25	0.08
$\sigma_I, \sigma_R{}^-$	−2.72	−0.69	0.5052	1.25	0.39
$\sigma_I, \sigma_R{}^+$	−1.61	−2.02	0.9997	0.04	0.01
Swain *et al.*[b]	−0.45	−1.11	0.9913	0.19	0.06
meta-substituted					
$\sigma_I, \sigma_R{}^0$	−2.37	−1.32	0.9966	0.06	0.06
$\sigma_I, \sigma_R{}^{BA}$	−2.33	−0.90	0.9838	0.12	0.14
$\sigma_I, \sigma_R{}^-$	−2.27	−0.86	0.9947	0.07	0.08
$\sigma_I, \sigma_R{}^+$	−2.25	−0.50	0.9690	0.17	0.19
Swain *et al.*[b]	−1.35	−0.34	0.9856	0.12	0.13

[a] SD = standard deviation, *R* = coefficient of multiple correlation, *f* = SD/(root mean square of log k/k_0); σ_I and σ_R are from ref. 19. [b] Field and resonance constants are from ref. 20.

V are field, resonance and steric substituent constants; the values used were those compiled by Aslam *et al.*[25]

$$\log k_{ortho} = \rho_I\sigma_I + \rho_R\sigma_R + h \tag{3}$$

$$\log k_{ortho} = \rho_I\sigma_I + \rho_R\sigma_R + \varphi V + h \tag{4}$$

The results of correlation in terms of eqn. (3) are given in eqn. (5), where *n* is the number of data points. In the multiple linear regression using eqn. (3), the correlation coefficient is poor and the standard deviation is high.

$$\log k = -2.39\,\sigma_I - 3.24\,\sigma_R - 4.68 \tag{5}$$

$$R = 0.9370;\ SD = 0.31;\ \psi = 0.25;\ n = 10$$

This showed that electrical effects alone are not sufficient to account for the observed *ortho*-effect in the oxidation of sulphides by LTA. Here ψ is Exner's statistical parameter.[26] According to Exner's[26] criterion also the correlation is poor.

Correlation in terms of eqn. (4) was performed assuming both orthogonal and planar conformations for the NO_2 and CO_2Me groups. The correlation was better with an orthogonal

Table 5 Temperature dependence of the reaction constants

T/K	ρ_I	ρ_R	λ^a	R	SD	f
para-substituted[b]						
288	−1.72	−1.98	1.15	0.9993	0.05	0.02
298	−1.61	−2.02	1.25	0.9997	0.04	0.01
308	−1.40	−1.94	1.38	0.9973	0.10	0.03
318	−1.28	−1.94	1.52	0.9998	0.03	0.01
meta-substituted[c]						
288	−2.50	−1.41	0.64	0.9964	0.06	0.07
298	−2.37	−1.32	0.64	0.9966	0.06	0.06
308	−2.31	−1.25	0.68	0.9980	0.04	0.05
318	−2.16	−1.18	0.65	0.9976	0.04	0.05

[a] $\lambda = \rho_R/\rho_I$. [b] No. of data points = 10. [c] No. of data points = 11.

conformation for both the groups. The results [eqn. (6)] showed that the correlation with eqn. (4) is just satisfactory.

$$\log k = 2.01\,\sigma_I - 3.35\,\sigma_R - 0.99\,V - 4.39 \qquad (6)$$

$$R = 0.9563;\ \mathrm{SD} = 0.24;\ \psi = 0.20;\ n = 10$$

Since the rates of the oxidation of *meta*- and *para*-substituted sulphides showed excellent correlation in Taft's DSP equation[19] with $\sigma_R{}^0$ and $\sigma_R{}^+$ respectively, the rates of the *ortho*-substituted sulphides were correlated in triparametric equations using Taft's σ_I and $\sigma_R{}^0/\sigma_R{}^+$, and Charton's steric parameters. Excellent correlation were obtained with Taft's σ_I and $\sigma_R{}^+$, and Charton's V values. The reaction constants and statistical data are recorded in Table 6. The behaviour of NO_2 and CO_2Me groups is consistent with their orthogonal conformations.

To test the significance of the three substituent constants, multiple linear regressions were carried out with Taft's σ_I and $\sigma_R{}^+$, Taft's σ_I and V, and $\sigma_R{}^+$ and V. The absence of significant correlations [eqns. (7)–(9)] showed that all the three substituent constants are significant.

$$\log k = -2.10\,\sigma_I - 1.65\,\sigma_R{}^+ - 4.68 \qquad (7)$$

$$R = 0.9707;\ \mathrm{SD} = 0.18;\ \psi = 0.15;\ n = 10$$

$$\log k = -3.54\,\sigma_I - 0.10\,V - 3.64 \qquad (8)$$

$$R = 0.6786;\ \mathrm{SD} = 1.01;\ \psi = 0.82;\ n = 10$$

$$\log k = -1.94\,\sigma_R{}^+ - 1.51\,V - 4.78 \qquad (9)$$

$$R = 0.9511;\ \mathrm{SD} = 0.42;\ \psi = 0.35;\ n = 10$$

There is no significant collinearity between Taft's σ_I and V, $\sigma_R{}^+$ and V, and Taft's σ_I and $\sigma_R{}^+$ ($R = 0.3519$, 0.0268 and 0.3592 respectively) for the ten substituents.

The regression coefficient of the σ_I and $\sigma_R{}^+$ terms are negative indicating that electron-releasing groups accelerate the reaction. The negative regression coefficient for the steric term indicates that the reaction is subject to steric retardation by the *ortho*-substituents. The contribution of the resonance parameter[24] to the total polar effect of the *ortho*-substituents was calculated using eqn. (10).

$$P_R = \frac{|\rho_R| \times 100}{|\rho_I| + |\rho_R{}^+|} \qquad (10)$$

The contribution of the steric parameter to the total effect of the substituents, P_S, was determined by using eqn. (11).[24]

$$P_S = \frac{100 \times |\varphi|}{|\rho_I| + |\rho_R{}^+| + |\varphi|} \qquad (11)$$

The values of P_R and P_S are also recorded in Table 6. P_R is *ca.* 48%. The value of P_R for the *para*-substituted compounds ranges from 53 to 60%. This shows that the balance of resonance and field effects is different for the *ortho* and *para* positions, the resonance effects being less pronounced in the former case. This may be due to twisting of the methylthio group away from the plane of the benzene ring. The value of P_S shows that there is a considerable steric effect in this reaction. Comparable studies of the oxidation of *ortho*-substituted aryl methyl sulphides by other oxidants are not available.

Analysis of the rates of oxidation of alkyl phenyl sulphides separately with Taft's σ^* and E_s values did not yield a satisfactory correlation. The rates were, therefore, analysed by the Pavelich–Taft[27] DSP equation (12).

$$\log k = \rho^*\,\sigma^* + \delta E_s + h \qquad (12)$$

The number of compounds (five) is rather small for an analysis by a biparametric equation but the correlations are excellent (Table 7) 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 reactivity of the alkyl phenyl sulphides may be compared with those observed in the oxidations by other reagents. The oxidations by peroxoanions[4] are hindered by the increasing bulk of the alkyl group and electron-donating effect of the alkyl groups does not have much effect. This may be due to the weak electrophilic nature of the oxidants. In the oxidation by chloroamine-T, the steric effects are almost completely absent, presumably due to the smaller size of the attacking Cl^+.[1a] The results obtained in this study are similar to those reported for the oxidation by periodate[9] and permanganate anion[10] *i.e.*, the electron-donating effect of the alkyl group enhances the rate greatly and the steric effects play a minor inhibitory role.

Mechanism.—The experimental results can be accounted for in terms of a rate-determining nucleophilic attack by the sulphide sulphur on LTA to yield a sulphonium cation. The large negative reaction constants and correlation of the rates of the *ortho*- and *para*-substituted compounds with $\sigma_R{}^+$ values indicate, in the transition state, a strong resonance interaction of the substituents in the aromatic ring with a developing positive charge at the sulphur centre. The greater susceptibility of the oxidation of *para*-compounds to resonance effects also points to a considerable cross-conjugation between the substituent and the reaction centre in the transition state. Thus the transition state approaches a sulphonium ion in character. The solvent

Table 6 Temperature dependence of the reaction constants for the oxidation of *ortho*-substituted phenyl methyl sulphides by LTA[a]

T/K	ρ_I	ρ_R	φ	R	ψ	SD	P_R	P_S
288	−1.92	−1.73	−0.82	0.9978	0.08	0.10	47.4	18.3
298	−1.83	−1.68	−0.81	0.9976	0.08	0.10	47.9	18.8
308	−1.78	−1.63	−0.77	0.9973	0.08	0.11	47.8	18.4
318	−1.71	−1.58	−0.75	0.9971	0.09	0.11	48.0	18.6

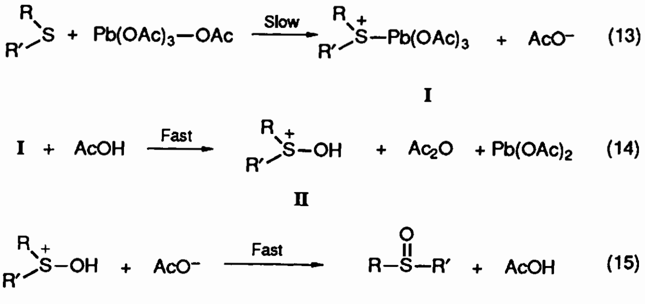
[a] No. of data points = 10 including that of the unsubstituted compounds.

Table 7 Correlation of rate of oxidation of alkyl phenyl sulphides with Pavelich–Taft equation[a]

T/K	ρ^*	δ	R	SD	ψ
288	−2.26	0.62	0.9993	0.01	0.04
298	−2.11	0.59	0.9979	0.02	0.08
308	−2.07	0.58	0.9972	0.02	0.09
318	−2.15	0.58	0.9981	0.01	0.08

[a] No of data points = 5.

effect also indicates a transition state more polarized than the reactant. Further, the value of m points to a considerable charge separation in the transition state or in other words a product-like transition state. There is a considerable steric interaction between the *ortho*-substituents and the reaction centre in the transition state. Similar interactions are operative in the oxidation of alkyl phenyl sulphides. Bulky *ortho*- and alkyl substituents hinder the approach of LTA to the sulphide sulphur. The steric interaction is reduced in groups capable of assuming an orthogonal conformation *i.e.*, NO_2 and CO_2Me. One can visualize a number of possible mechanisms involving nucleophilic attack on LTA to yield a sulphonium cation intermediate. In the oxidation of bicyclic disulphides by LTA, Trost *et al.*[28] have proposed the formation of a sulphonium cation possessing a sulphur–lead bond. In view of this, the following mechanism is proposed [eqns. (13)–(15)].



Reaction (14) is not likely to be a single-step process and is probably composed of several fast steps. The intermediate **I** does not undergo any rearrangement of the carbon skeleton as found by Trost *et al.*[28] This may be because of the diverse nature of the carbon skeletons. The sulphides used by Trost *et al.*[28] were bicyclic disulphides (with sulphur atoms being part of a ring) bearing a tertiary alcoholic group on the β carbon atom. The sulphides used in this investigation, on the other hand, were simple aryl alkyl ones and were devoid of any other functional group. There is no experimental evidence for the formation of a protonated sulphoxide intermediate (**II**) subsequent to the rate-determining step, though the formation of intermediates like **II** has been reported by several earlier workers.[1,2] The formation of acetic anhydride was confirmed by a spot test.[29]

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