JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 3, 174–180 (1989)

KINETICS AND MECHANISM OF THE OXIDATION OF ORGANIC SULPHIDES BY *N*-CHLOROACETAMIDE

ANUPMA AGARWAL, PALLAVI BHATT AND KALYAN K. BANERJI*
Department of Chemistry, University of Jodhpur, Jodhpur 342 001, India

The kinetics of the oxidation of a number of monosubstituted aryl methyl, alkyl phenyl, dialkyl and diphenyl sulphides by *N*-chloroacetamide (NCA) to yield the corresponding sulphoxides were studied. The reaction is first order with respect to the sulphide, NCA and hydrogen ions. There is no effect of added acetamide. Protonated NCA has been postulated as the reactive oxidizing species. 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*-substituted compounds, the best correlation is obtained with σ_I and σ_R^+; the *meta*-substituted compounds correlate best with σ_I and $\sigma_R{}^0$ values. The reaction constants are negative. The oxidation rates of the *ortho*-substituted sulphides yield an excellent correlation in a triparametric equation involving Taft's σ_I and σ_R^+ values and Charton's steric parameter, *V*. The oxidation of alkyl phenyl sulphides is susceptible to both polar and steric effects of the alkyl group. A mechanism involving the formation of a halogenosulphonium cation in the rate-determining step is proposed.

INTRODUCTION

The kinetics and mechanism of oxidations by *N*-bromoacetamide (NBA) have received considerable attention in recent years.[1–5] The kinetics of the sulphides by NBA[5] is complex. It has been proposed[5] that both NBA and the substrate form complexes with Hg^{II}. On the other hand, there seems to be no report on oxidations by *N*-chloroacetamide (NCA). Oxidations by *N*-chlorosuccinimide[7] are reported to follow different mechanisms. In view of the lack of information about the mechanism of oxidations by NCA, the mechanism of the oxidation of organic sulphides by NCA has been studied by kinetic methods. Correlation analysis of the reactivity has also been attempted.

RESULTS

The oxidation of organic sulphides by NCA results in the formation of corresponding sulphoxides:

$$R{-}S{-}R' + MeCONHCl + H_2O \rightarrow R{-}\underset{\underset{O}{\|}}{S}{-}R' + MeCONH_2 + HCl \qquad (1)$$

Rate laws

The oxidation of sulphides by NCA is first order with respect to NCA. Further, the pseudo-first-order rate constants, k_{obs}, do not depend on the initial concentration of NCA. The variation in the concentration of the sulphide indicates that the reaction is first order with respect to the sulphide also. The reaction rate increases linearly with an increase in the hydrogen ion concentration (Table 1).

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

[MeSPh] (M)	10^3[NCA] (M)	[H$^+$] (M)	$10^6 k_{obs}$(s^{-1})
0·5	2·5	1·0	5·42
0·5	5·0	1·0	5·35
0·5	7·5	1·0	5·40
0·5	10·0	1·0	5·20
0·5	15·0	1·0	5·30
0·2	5·0	1·0	2·17
0·8	5·0	1·0	8·45
1·0	5·0	1·0	10·8
1·4	5·0	1·0	15·0
1·7	5·0	1·0	18·0
2·0	5·0	1·0	21·1
1·0	5·0	0·3	3·30
1·0	5·0	0·6	6·42
1·0	5·0	1·2	13·0
1·0	5·0	1·5	15·8
1·0	5·0	1·8	19·3
1·0	5·0	2·1	22·6

0894–3230/90/030174–07$05.00

Received 5 January 1989
Revised 8 April 1989

Table 2. Effect of acetamide on the oxidation of MeSPh by NCA[a]

10^3[Acetamide] (M)	0·0	2·5	5·0	10·0	15·0	20·0
$10^6 k_{obs}(s^{-1})$	10·8	10·6	11·0	10·8	11·1	11·0

[a] [MeSPh] 1·0 M; [NCA]0·005 M; [H^+]1·0 M; Temperature 298 K.

Table 3. Effect of solvent composition on the oxidation rate[a]

Acetic acid (% v/v)	30	50	60	70	80
10^6 $k_{obs}(s^{-1})$	8·36	10·8	15·5	25·7	40·3

[a] [MeSPh] 1·0 M; [NCA]0·005 M; [H^+]1·0 M; Temperature 298 K.

Effect of acetamide

Added acetamide has no effect on the rate of reaction (Table 2).

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 reaction decreases as the amount of water in the solvent is increased (Table 3).

Effect of substituents

The rates of oxidation of a number of *ortho*-, *meta*- and *para*-substituted phenyl methyl sulphides, alkyl phenyl

Table 4. Rate constants at different temperatures and activation parameters of the oxidation of sulphides by NCA

	$10^7 k_2 (l^2\ mol^{-2} s^{-1})$				ΔH^*	ΔS^*	ΔG^*
Substituent	288 K	298 K	308 K	318 K	(kJ mol^{-1})	(J $mol^{-1} K^{-1}$)	(kJ mol^{-1})
			(i) Aryl methyl sulphides				
H	42·4	107	271	620	65·8	−119	101
p-Me	139	301	635	1560	58·3	−135	98·1
p-OMe	1050	2530	5780	11200	57·9	−119	94·6
p-F	100	211	472	1100	58·3	−138	99·6
p-Cl	45·0	113	283	651	65·5	−119	101
p-Br	28·0	85·6	250	565	74·7	−92	102
p-NO_2	2·79	9·63	25·4	77·7	80·9	−89	107
p-COMe	10·0	27·1	73·0	165	70·7	−113	105
p-COOMe	10·7	29·0	78·2	190	69·1	−119	105
p-NH_2	29500	51600	93700	147000	38·7	−158	86·0
m-Me	72·0	171	397	870	60·8	−132	100
m-OMe	38·1	98·0	252	593	67·4	−114	101
m-NH_2	75·7	187	454	1030	63·9	−121	100
m-Cl	11·8	29·1	71·5	163	64·3	−135	104
m-Br	9·64	26·5	73·0	181	72·2	−109	105
m-I	12·2	33·3	90·0	217	70·8	−104	104
m-NO_2	1·37	4·45	14·5	41·5	84·4	−83	109
m-COOMe	7·72	21·5	58·5	147	72·4	−110	105
o-Me	19·2	53·5	145	349	71·3	−107	103
o-OMe	356	856	1950	4140	59·8	−123	96·2
o-NO_2	043	1·17	3·36	9·10	75·2	−126	112
o-COOMe	1·63	4·24	12·1	30·0	72·0	−126	109
o-NH_2	2040	5650	10700	20400	55·1	−124	91·9
o-Cl	3·26	7·62	17·0	51·6	66·5	−139	108
o-Br	2·42	6·60	17·1	34·5	65·5	−144	108
o-I	2·95	6·66	21·0	49·3	70·5	−126	108
o-CN	1·47	2·05	5·35	15·2	57·5	−177	110
			(ii) Alkyl phenyl sulphides				
Et	68·2	167	400	1000	65·4	−117	100
n-Pr	40·1	88·6	252	565	65·8	−121	102
i-Pr	46·1	108	313	875	72·7	−96	101
t-Bu	8·02	25·3	56·4	170	73·3	−107	105
			(iii) Other sulphides				
Me_2S	105	274	578	1370	61·8	−125	99·2
Pr_2S	264	630	1520	3110	60·6	−122	96·9
Ph_2S	22·0	56·5	160	386	70·8	−107	103

sulphides, dialkyl sulphides and diphenyl sulphide were determined at different temperatures and the activation parameters were calculated (Table 4).

DISCUSSION

A linear isokinetic relationship exists between log k_2 at 288 K and log k_2 at 381 K (slope = 0·8890 ± 0·016, $r = 0.9948$) for the oxidation of 34 sulphides. This suggests that all the sulphides are oxidized by the same mechanism.[8] The value of isokinetic temperature is 1919 ± 115 K.

The oxidation of sulphides[5] by NBA was carried out in the presence of HG^{II}. Hg^{II} was added to prevent the liberation of bromine by trapping the bromide ions formed, in the form of complexes.[1] It has been reported that Hg^{II} forms complexes with both NBA and the sulphide and these complexes participate in the rate-determining step.[5] However, in no other reaction of *N*-bromoamides has the formation and participation of such complexes in the oxidation process been reported.[1–4,6] In the oxidations by *N*-chloroamides,[7] addition of Hg^{II} is not necessary as liberation and further reactions of chlorine have not been observed.

N-Halogenoamides are known to hydrolyse/disproportionate to yield hypohalous acid.[1,2,6] Hypohalous acids and their protonated forms have been postulated as reactive species in many reactions.[1,2,6] However, no effect of added acetamide precludes a pre-equilibrium in which acetamide is one of the products. This in effect rules out the involvement of hypochlorous acid in the oxidation process. Hence it seems that in the present reaction, NCA itself is the reactive oxidizing species. This is in sharp contrast to the observations in NBA oxidations,[1–5] where hypobromous acid has been postulated as the reactive oxidizing species and a decrease in the reaction rate on the addition of acetamide was observed.

The linear increase in the reaction rate with acidity suggests the protonation of NCA to give a stronger oxidant and electrophile:

$$\mathrm{MeCONHCl} + \mathrm{H_3O^+} \rightleftharpoons (\mathrm{MeCONH_2Cl})^+ + \mathrm{H_2O} \qquad (2)$$

The fact that no levelling in the reaction rate was observed, even at high acidity, indicates that the protonation constant is small. The equilibrium constant of reaction (2) was not determined.

The decrease in the reaction rate with increase in the water content of the solvent indicates that a decrease in the polarity of the solvent favours the reaction. Thus the transition state of the reaction is less polar than the reactants. This accords with the postulation of (NCAH)$^+$ as the reactive oxidizing species. When (NCAH)$^+$ and the sulphide react, the charge is spread over a wider area in the transition state; the charge density is thus reduced. The decreased polarity of the transition state is facilitated by the low polarity of the solvent. This also accords with the postulation of a protonation of a neutral species in the pre-equilibrium.

Correlation analysis of reactivity

The data in Table 4 show that the oxidation of different sulphides follows the order of their nucleophilicity: $\mathrm{Pr_2S} > \mathrm{Me_2S} > \mathrm{MeSPh} > \mathrm{Ph_2S}$.

The oxidation rates of *meta*- and *para*-substituted phenyl methyl sulphides failed to show satisfactory correlation with any single substituent-parameter equation. The rates for the *meta*- and *para*-substituted compounds were therefore subjected to analysis in terms of Taft's[9] and Swain's[10] dual substituent parameter (DSP) equations. The rates for the *para*-substituted sulphides show an excellent correlation with σ_I and σ_R^+ values (Table 5). We used the standard deviation (SD), coefficient of multiple correlation (R), and the parameter f as measures of goodness of fit; f has been defined[9] 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 5–9. Thus it is apparent that the rates of the oxidation of *para*-substituted phenyl methyl sulphides by NCA correlate best with σ_I and σ_R^+.

The rates of the oxidation of the *meta*-compounds show excellent correlation with σ_I and σ_R^0, although the discriminating factor for the precision of fit with the other σ 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 ($f < 0{\cdot}1$). This agrees with the observation of Ehrenson *et al.*[11] that the correlation of *meta*-substituted compounds is generally best with σ_R^0 and *meta*-substituted compounds are less discriminating.

The reaction constants and statistical data at different

Table 5. Correlation of the rates of oxidation of *para*- and *meta*-substituted phenyl methyl sulphides by NCA at 298 K[a]

Substituent constants	ρ_I	ρ_R	R	SD	f
	para-Substituted				
σ_I, σ_R^0	−1·80	−3·63	0·9303	0·45	0·42
σ_I, σ_R^{BA}	−1·60	−2·80	0·9795	0·25	0·23
σ_I, σ_R^-	−1·55	−2·14	0·8527	0·64	0·60
σ_I, σ_R^+	−1·30	−1·71	0·9992	0·05	0·05
Swain *et al*·[6]	−0·33	−0·93	0·9858	0·21	0·21
	meta-Substituted				
σ_I, σ_R^0	−1·83	−1·03	0·9987	0·03	0·05
σ_I, σ_R^{BA}	−1·82	−0·68	0·9886	0·09	0·15
σ_I, σ_R^-	−1·67	−0·76	0·9861	0·10	0·17
σ_I, σ_R^+	−1·82	−0·36	0·9789	0·12	0·19
Swain *et al*·[6]	−1·04	−0·28	0·9898	0·09	0·15

[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. 9.

[b] Field and resonance constants are from Ref. 10

Table 6. Temperature dependence of the reaction constants

Temperature (K)	ρ_I	ρ_R	λ[a]	R	SD	f
		para-Substituted[b]				
288	−1·45	−1·81	1·25	0·9986	0·07	0·06
298	−1·30	−1·71	1·32	0·9992	0·05	0·05
308	−1·20	−1·64	1·37	0·9988	0·06	0·06
318	−1·11	−1·54	1·39	0·9985	0·04	0·04
		meta-Substituted[c]				
288	−1·96	−1·10	0·56	0·9969	0·05	0·08
298	−1·83	−1·03	0·56	0·9987	0·03	0·05
308	−1·71	−0·96	0·56	0·9994	0·02	0·03
318	−1·60	−0·88	0·55	0·9989	0·03	0·04

[a] $\lambda = \rho_R/\rho_I$.
[b] No. of data points = 10.
[c] No. of data points = 9.

temperatures are recorded in Table 6. The value of λ^p (1·25–1·39) showed that the oxidation of the *para*-substituted sulphides is more susceptible to resonance effect than to the field effect. In the oxidation of the substituted compounds, however, the value of λ^m is ca 0·56, 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 *p*-substituted 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*-substituted compounds, the decreases in the two reaction constants are of similar order, resulting in an almost constant value of λ^m.

In none of the earlier reports on the oxidation of sulphides, DSP equations have been used for correlating the effect of structures on reactivity. In oxidations by reagents which involved a direct oxygen transfer via an electrophilic attack on the sulphide sulphur, the reaction constants are negative but are relatively small, e.g. hydrogen peroxide (−1·13),[12] periodate (−1·40),[13] permanganate (−1·52)[14] and peroxydisulphate (−0·56).[15] The reactions involving the 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,[16] bromine[17] and NBA[5], respectively). In this study, the total effects of the *meta* and *para* substituents have been dissected into contributions by inductive and resonance effects. The reaction constants are large and negative. Hence the formation of a strongly electron-deficient sulphur centre in a transition state is indicated.

The rates of the oxidation of *ortho*-substituted phenyl methyl sulphides failed to yield any significant correlation with either Taft's polar or steric substituent constants.[18] The rates were, therefore, analysed by Charton's method.[19] The rates were analysed using equations (2) and (3), where σ_I, σ_R and V are field, resonance and steric substituent constants, respectively; the values used were those compiled by Aslam *et al.*[20]

$$\log k_{ortho} = \alpha\sigma_I + \beta\sigma_R + h \qquad (3)$$

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

The results of correlation in terms of equation (3) are given in the equation

$$\log k_2 = -2{\cdot}53\sigma_I - 3{\cdot}04\sigma_R - 5{\cdot}40 \qquad (5)$$

$$r = 0{\cdot}9284;\ \mathrm{SD} = 0{\cdot}56;\ n = 10$$

where n is the number of data points. In the multiple linear regression using equation (3), the correlation coefficient is poor and the standard deviation is high. This showed that electrical effects alone are not sufficient to account for the observed *ortho* effect in the oxidation of sulphides by NCA.

Correlation in terms of equation (4) was performed assuming both orthogonal and planar conformation for NO_2 and COOMe groups. The correlation was better with an orthogonal conformation of both the groups. The results [equation (5)] showed that the correlation with equation (4) is not very significant.

$$\log k_2 = -2{\cdot}21\sigma_I - 2{\cdot}58\sigma_R - 1{\cdot}11V - 5.01 \qquad (6)$$

$$r = 0{\cdot}9586;\ \mathrm{SD} = 0{\cdot}43;\ n = 10$$

Since the rates of the oxidation of *meta*- and *para*-substituted sulphides showed excellent correlation in Taft's DSP equation[9] with σ_R^0 and σ_R^+, respectively, the rates for the *ortho*-substituted sulphides were correlated in triparametric equations using Taft's σ_I and σ_R^0/σ_R^+ and Charton's steric parametrs. Excelent correlatin were obtained with Taft's σ_I and σ_R^+ and Charlton's V values. The reaction constants and statistical data are given in Table 7. The behaviour of NO_2 and COOMe groups is consistent with their orthogonal conformations.

To test the significance of the three substituent constants, multiple linear regressions were carried out with

Table 7. Temperature dependence of the reaction constants for the oxidation of *ortho*-substituted phenyl methyl sulphides by NCA[a]

Temperature (K)	ρ_I	ρ_R	ϕ	R	SD	P_R	P_S
288	$-1\cdot64$	$-1\cdot56$	$-1\cdot35$	$0\cdot9894$	$0\cdot21$	$48\cdot8$	$29\cdot7$
298	$-1\cdot81$	$-1\cdot60$	$-1\cdot28$	$0\cdot9944$	$0\cdot15$	$46\cdot9$	$27\cdot3$
308	$-1\cdot86$	$-1\cdot49$	$-1\cdot16$	$0\cdot9917$	$0\cdot18$	$45\cdot0$	$25\cdot7$
318	$-1\cdot75$	$-1\cdot43$	$-1\cdot19$	$0\cdot9924$	$0\cdot17$	$45\cdot0$	$27\cdot2$

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

Taft's σ_I and σ_R^+, Taft's σ_I and V, and σ_R^+ and V. The absence of significant correlations [equations (7)–(9)] showed that all the three substituent constants are significant.

$$\log k_2 = -2\cdot24\sigma_I - 1\cdot52\sigma_R^+ - 5\cdot41 \qquad (7)$$

$$r = 0\cdot9438;\ \mathrm{SD} = 0\cdot32;\ n = 10$$

$$\log k_2 = -3\cdot54\sigma_I - 0\cdot11V - 4.43 \qquad (8)$$

$$r = 0\cdot6992;\ \mathrm{SD} = 0\cdot97;\ n = 10$$

$$\log k_2 = -1\cdot84\sigma_R^+ - 1\cdot98V - 5.34 \qquad (9)$$

$$r = 0\cdot8974;\ \mathrm{SD} = 0\cdot43;\ n = 10$$

There is no significant collinearity between Taft's σ_I and V, σ_R^+ and V, and Taft's σ_I and σ_R^+ ($r = 0\cdot3519$, $0\cdot0268$ and $0\cdot3592$ respectively).

The regression coefficients of the σ_I and σ_R^+ terms are negative, indicating that electron-releasing groups accelerate the reaction. The negative regression coefficients for the steric term indicates that the reaction is subject to steric retardation by the *ortho* substituents. The contribution of the resonance parameter[20] to the total polar effect of the *ortho* substituents was calculated using the equation

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

The contribution of the steric parameter to the total effect of the substituents, P_S, was determined by using the equation[20]

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

The values of P_R and P_S are also given in Table 7; P_R is ca 46%. The value of P_R for the *para*-substituted compounds ranges from 55 to 58%. This shows that the balance of resonance and field effects is different for *ortho* and *para* positions, the resonance effects being less pronounced in the former case. This may be due to twisting away of the methylthio group from the plane of the benzene ring. The value of P_S shows that there is considerable steric effect in this reaction. Comparable studies involving *ortho*-substituted aryl methyl sulphides are not available

Table 8. Correlation of rate of oxidation of alkyl phenyl sulphides in the Pavelich–Taft equation[a]

Temperature (K)	ρ^*	δ	R	SD
288	$-2\cdot60$	$0\cdot98$	$0\cdot9996$	$0\cdot02$
298	$-2\cdot16$	$0\cdot83$	$0\cdot9977$	$0\cdot03$
308	$-2\cdot65$	$0\cdot95$	$0\cdot9988$	$0\cdot02$
318	$-3\cdot12$	$0\cdot96$	$0\cdot9966$	$0\cdot04$

[a] No. of data points = 5.

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[21] DSP equation:

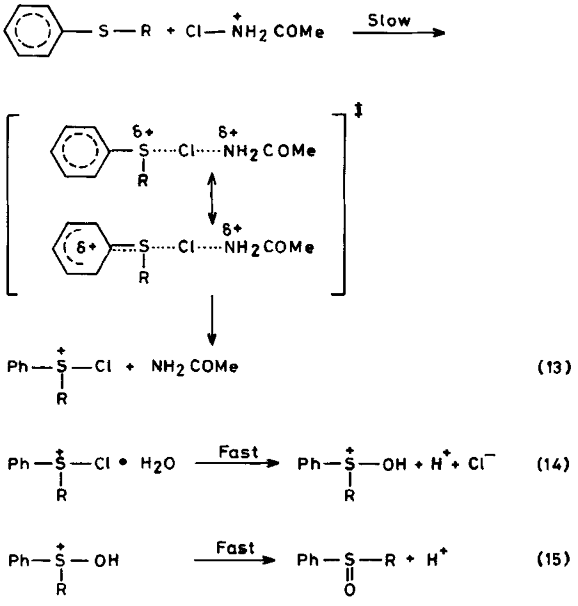
$$\log k = \rho^*\sigma^* + \delta E_S + h \qquad (12)$$

The number of compounds (five) is small for an analysis by a biparametric equation, but the correlations are excellent (Table 8) 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 oxidation by other reagents. The oxidations by peroxoanions[15,22] are hindered by the increasing bulk of the alkyl group and the $+I$ 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 chloramine-T, the steric effects are almost completely absent, presumably owing to the smaller size of the attacking Cl^+.[18] The results obtained in this study are similar to those reported for the oxidation by periodate and permanganate anion, i.e. the $+I$ 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 electrophilic attack of a protonated NCA molecule on the sulphide to yield a halogenosulphonium ion, similar to those suggested for the oxidations of sulphides by bromamine-B[23] and halogens.[17] The large negative reaction constants and correlation of the rates of the *ortho*- and *para*-substituted compounds with σ^+ values indicated, in the transition state, a strong resonance interaction of the substituents in the aromatic ring with a developing positive charge at the sulphur centre. There is a considerable steric interaction also between the *ortho* substituents and the reaction centre in the transition state. The steric interaction is reduced in groups capable of assuming orthogonal conformation, i.e. NO_2 and COOMe. One can visualize the mechanism shown in Scheme 1 for the reaction.



Scheme 1

EXPERIMENTAL

Materials. The sulphides were either commercial products or prepared by known methods,[13,24–29] and were purified by distillation under reduced pressure or crystallization. Their purity was checked by comparing their boiling or melting points with the literature values. NCA was prepared by the reported method.[30] Acetic acid was refluxed over chromic oxide for 6 h and then fractionated.

Product analysis. Methyl phenyl sulphide (0·005 mol) and NCA (0·005 mol) were dissolved in 1 : 1 (v/v) acetic acid–water (40 ml) in the presence of perchloric acid (0·002 mol) 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 extracted with chloroform (3 × 50 ml). The chloroform layer 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 $MeOP_2Ph$ 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 NCA. The reactions were carried out at constant temperature (±0·05 K). The solvent was 1 :1 (v/v) acetic acid–water unless stated otherwise. Preliminary experiments showed that the reaction is not sensitive to ionic strength (0.05–2.5 M), hence no attempt was made to keep the ionic strength constant. The reactions were followed iodimetrically for up to 70% of the extent of reaction. The observed rate constant, k_{obs}, was determined from the linear plots of log[NCA] against time. The third-order rate constant, k_2, was obtained from the relation $k_2 = k_{obs}/[\text{sulphide}][\text{H}^+]$. Duplicate kinetic runs showed that the rates were reproducible to within ±3%.

ACKNOWLEDGEMENTS

Thanks are due to CSIR (India) for financially supporting the project. Thanks are also due to the referees for valuable suggestions.

REFERENCES

1. J. Mukherjee and K. K. Banerji, *J. Org. Chem.* **46**, 2323 (1981); S. C. Negi and K. K. Banerji, *Indian J. Chem., Sect. B* **21**, 846 (1982); I. Bhatia, S. C. Negi and K. K. Banerji, *J. Chem. Res.* (*S*) 360 (1981); (*M*) 3966 (1981); V. Sharma and K. K. Banerji, *J. Chem. Res.* (*S*) 540 (1985); (*M*) 3551 (1985).
2. M. Jambulingam, P. Nanjappan and K. Natarajan, *J. Chem. Soc., Perkin Trans. 2* 1699 (1985).
3. B. Shah and K. K. Banerji, *J. Chem. Soc., Perkin Trans. 2* 33 (1983).
4. S. C. Negi and K. K. Banerji, *J. Org. Chem.* **48**, 3329 (1983).
5. S. Perumal, S. Alagumalai, S. Selvaraj and N. Arumugam, *Tetrahedron* **42**, 4867 (1986).
6. N. Venkatasubramanian and V. Thiagarajan, *Tetrahedron Lett.* 3349 (1967).
7. V. S. Srinivasan and N. Venkatasubramanian, *Tetrahedron* **30**, 319 (1974).
8. O. Exner, *Collect. Czech. Chem. Commun.* **29**, 1094 (1964).
9. S. K. Dayal, S. Ehrensen and R. W. Taft, *J. Am. Chem. Soc.* **94**, 9113 (1974).
10. C. S. Swain, S. H. Unger, N. R. Rosenquest and M. S. Swain, *J. Am. Chem. Soc.* **105**, 492 (1983).
11. S. Ehrensen, R. T. C. Brownlee and R. W. Taft, *Prog. Phy. Org. Chem.* **10**, 1 (1973).

12. G. Modena and L. Maioli, *Gazz. Chim. Ital.* **87**, 1306 (1957).
13. F. Ruff and A. Kucsman, *J. Chem. Soc., Perkin Trans. 2* 683 (1985)
14. K. K. Banerji, *Tetrahedron* **44**, 2969 (1988)
15. C. Srinivasan, P. Kuthalingam and N. Arumugam, *Can. J. Chem.* **56**, 3043 (1978).
16. F. Ruff and A. Kucsman, *J. Chem. Soc., Perkin Trans. 2* 509 (1975).
17. U. Miotti, G. Modena, and L. Sadea, *J. Chem. Soc. B* 802 (1975).
18. R. A. Y. Jones, *Physical and Mechanistic Organic Chemistry*, pp. 52–60. Cambridge University Press, Cambridge (1979).
19. M. Charton, *J. Org. Chem.* **40**, 407 (1975).
20. M. H. Aslam, A. G. Burden, N. B. Chapman, J. Shorter and M. Charton, *J. Chem. Soc., Perkin Trans. 2* 500 (1981).
21. W. H. Pavelich and R. W. Taft, *J. Am. Chem. Soc.* **79**, 4935 (1956).
22. C. Srinivasan, P. Kuthalingam and N. Arumugam, *J. Chem. Soc., Perkin Trans. 2* 170 (1980).
23. F. Ruff, K. Komoto, N. Furoukawa and S. Oae, *Tetrahedron* **32**, 2763 (1976).
24. C. Srinivasan, P. Kuthalingam, A. Chelamani, S. Rajagopal and N. Arumugam, *Proc. Indian Acad. Sci., Chem. Sci.,* **95**, 157 (1984).
25. T. Zuncke and H. Swartz, *Chem. Ber.* **46**, 775 (1913); **48**, 1242 (1915).
26. A. W. Hofmann, *Chem. Ber.* **20**, 2260 (1887).
27. H. Gilman and G. C. Gainer, *J. Am. Chem. Soc.* **71**, 1747 (1949).
28. A. J. Saggiomo, P. N. Craig and M. Gordon, *J. Org. Chem.* **23**, 1906 (1958).
29. E. A. Nodiff, S. Lipschutz, P. N. Craig and M. Gordon, *J. Org. Chem.* **25**, 60 (1960).
30. G. H. Coleman, R. L. Petersen and G. E. Goheen, *J. Am. Chem. Soc.* **58**, 1874 (1936).