The Oxygen Exchange between Sulphoxides and Sulphides. The Hydrogen Chloride Catalysed Reaction between *p*-Chlorophenyl Methyl Sulphoxide and Dibutyl Sulphide [1,2]

By **Annamaria Bovio** and **Umberto Miotti,*** Centro ' Meccanismi di Reazioni Organiche ' del C.N.R., Istituto di Chimica Organica, Universitá di Padova, 35100 Padova, Italy

Alkyl aryl sulphoxides are reduced by dialkyl sulphides in 2 : 1 methanol–water in the presence of 4M-HCl. The kinetics of the reaction between *p*-chlorophenyl methyl sulphoxide and dibutyl sulphide and the basic properties of the sulphoxide have been investigated in detail. Reaction orders, acid catalysis, and comparison of the reduction rate with that of the loss of optical activity by the (+)-*R*-sulphoxide indicate a predominant role for the chlorosulphonium cation. A mechanism is suggested in which the changes of the oxidation states occur through the reaction between the sulphide and this intermediate.

THE chemistry of sulphoxides has been the subject of a number of mechanistic studies in these laboratories. We were attracted by a reaction of some theoretical and synthetic interest, namely oxygen transfer from sulphoxides to organic sulphides. This reaction has been reported to occur [3-8] particularly well in the presence of HCl,[9-11] other acids such as H_2SO_4 or $HClO_4$ being much less effective catalysts; the reaction is strongly dependent on the structure of the reactants. The only related mechanistic study so far published [8] deals with intramolecular oxygen migration from *o*-alkylthiophenyl aryl sulphoxides to a sulphide sulphur in 70—80% H_2SO_4. In the light of our earlier hypothesis,[2] our interest was stimulated by the idea that catalysis by HCl of the oxygen exchange reaction is mechanistically related to the effective oxidising and halogenating abilities of the sulphoxide–hydrogen halide system.[12-15]

We present here a kinetic study of the HCl catalysed reaction between *p*-chlorophenyl methyl sulphoxide (Ia) and dibutyl sulphide (IId), an equilibrium which because it is almost completely shifted towards the products and is virtually irreversible under suitable concentration conditions, offers considerable advantages for kinetic investigation.

$$\underset{\text{(I)}}{\text{ArMeSO}} + \underset{\text{(II)}}{\text{R}_2\text{S}} \overset{\text{HCl}}{\rightleftharpoons} \underset{\text{(III)}}{\text{ArMeS}} + \underset{\text{(IV)}}{\text{R}_2\text{SO}} \qquad (1)$$

a; Ar = p-ClC_6H_4
b; Ar = p-$CH_3C_6H_4$
c; Ar = Ph
d; R = Bu^n
e; R = Bu^i

RESULTS

Products.—Sulphides and sulphoxides were identified and determined by g.l.c.; other products beside those of equation (1) were not identified. Experiments carried out under semipreparative conditions in MeOH–H_2O (2 : 0.75 v/v) at 25 °C showed the following features. (i) Sulphoxide (Ib) (0.03M) reacts in the presence of 4.1M-HCl with sulphide (IId) (0.02M) to form the aryl methyl sulphide (IIIb) and dibutyl sulphoxide (IVd). The reaction was virtually complete in 2 h but small amounts of the reactant sulphide were still present after a much longer time. This analysis allowed an estimate of a lower limit of 200 for the equilibrium constant. Similar results were obtained for the reaction between sulphoxide (Ia) and sulphide (IIe). Under the reaction conditions each individual reactant was stable. (ii) Sulphide (IIIb) reacts with (Ic) to give an equilibrium identical with that obtained from (IIIc) and (Ib). The equilibrium constants are 2.2 ± 0.1 and 0.44 ± 0.02 for the forward and the reverse reaction respectively. (iii) Exchange is not observed in the absence of acid catalyst. Perchloric and sulphuric acid in aqueous methanol or dioxan solution (*ca.* 4M) catalyse oxygen exchange but at a much lower rate; different kinetic features are observed however and these will be reported later.

The stoicheiometry of the reaction of (Ia) and (IId) was checked for the conditions of the kinetic experiments. The u.v. spectra at 230 nm of authentic samples of (IIIa or b) (both 5×10^{-5}M) recorded for a solution of (IId) (5×10^{-3}M) in aqueous methanolic HCl, corresponded to that of (Ia or b) (5×10^{-5}M) after 24 h under the same conditions; the contribution of (IVd) to the absorbance is negligible in this region.

Kinetics.—The reaction between *p*-chlorophenyl methyl sulphoxide and dibutyl sulphide was studied in MeOH–H_2O (2 : 1 and 2 : 0.75 v/v) in the presence of HCl and HCl–$HClO_4$ mixtures over the concentration range 2.9—5.2M. The rate constants $k_{obs.}$ were measured spectrophotometrically under pseudo-first-order conditions (the concentrations of reactant sulphoxide and sulphide were in the range 4.5×10^{-6}—5×10^{-5} and 2×10^{-5}—5×10^{-3}M,

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[1] Taken from the doctoral Thesis of A. Bovio, University of Padua, 1973.

[2] Some of the results have been presented by G. Modena, 5th International Symposium on Organic Sulfur Chemistry, Lund, 1972; *Internat. J. Sulfur Chem., C* 1972, **7**, 95.

[3] S. Searles and H. R. Hays, *J. Org. Chem.*, 1958, **23**, 2028.

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[9] A. Bortoli, Doctoral Thesis, University of Padua, 1970; unpublished results.

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[13] H. Gilman and J. Eisch, *J. Amer. Chem. Soc.*, 1955, **77**, 3862.

[14] T. L. Fletcher, M. J. Namkung, and Hsi-Lung Pan, *Chem. and Ind.*, 1957, 660.

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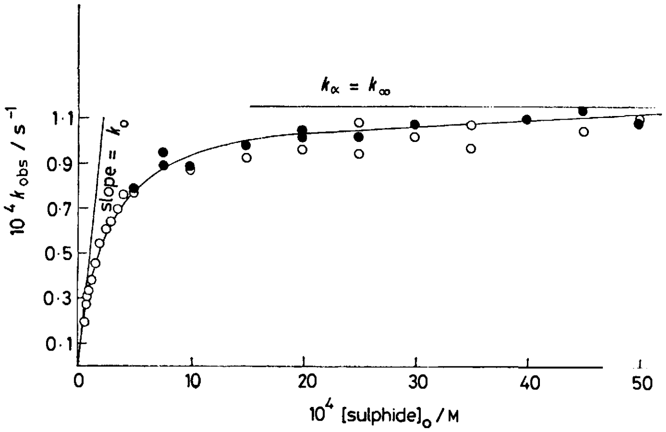
respectively) following the appearance of absorption corresponding to *p*-chlorophenyl methyl sulphide at 258 nm. In each run the first-order rate law was obeyed and the values of $k_{\mathrm{obs.}}$ were independent of the initial concentration of sulphoxide; this indicated the first-order dependence of the rate on the latter. On the other hand the effect of a change in the initial concentration of sulphide on the rate is quite different as shown in the Figure. The rate increase is linear at the lowest concentrations and then diminishes up to the point [sulphide] ⩾ 10^{-3}M where $k_{\mathrm{obs.}}$ is virtually independent of the sulphide concentration. The data fit equation (2) and indicate a gradual change from first to zero kinetic order in sulphide on increasing the concentration. According to equation (2) a linear plot of $1/k_{\mathrm{obs.}}$ against $1/[\mathrm{sulphide}]_0$ is obtained (correlation coefficient r 0.998) and the best values of the intercept a and the slope b obtained by the least-squares method, allow a calculation of the rate coefficients for the limiting situations when the reaction is zero and first order in sulphide. This gives $1/a = k_\infty = 1.14 \times 10^{-4}$ s^{-1} and $1/b = k_0 = 0.47$ l mol^{-1} s^{-1}. For the experimental conditions used k_∞ equals that of k_α, the polarimetric rate constant for loss of optical activity of the (+)-*R*-sulphoxide (see Table 1). Moreover, k_α is also unaffected by the presence of sulphide.



First-order rate coefficients for the reaction between *p*-chlorophenylmethyl sulphoxide and dibutyl sulphide at 25 °C in MeOH–H_2O (2 : 0.75 v/v) in the presence of [HCl] 4.11 ± 0.01M: ● [sulphoxide]$_0$ 5 × 10^{-5}M; ○ [sulphoxide]$_0$ 5 × 10^{-6}M

$$1/k_{\mathrm{obs.}} = a + b/[\mathrm{sulphide}]_0 \qquad (2)$$

TABLE 1

First-order rate coefficients for the HCl-catalysed reaction between *p*-chlorophenyl methyl sulphoxide and di-n-butyl sulphide at 25 °C in MeOH–H_2O (2 : 0.75 v/v)

10^4[sulphoxide]/M	0.5	0.05	0.5	100 [a]	100 [a]	100 [a]	100 [a]
10^4[sulphide]/M	50	50	50		50		50
10^4k_{obs}/s^{-1}	1.07	1.09	1.20	1.25	1.26	1.34	1.35
[HCl]/M	4.11	4.11	4.15	4.15	4.15	4.20	4.20

[a] See text. k_α determinated polarimetrically for the (+)-*R*-sulphoxide.

Protonation of p-*Chlorophenyl Methyl Sulphoxide and Acid Catalysis*.—The effect of a change in the medium acidity on the rate has been studied by experiments in which the concentration of HCl was kept constant (0.98M) and $HClO_4$ was added in variable amounts (1.88—4.24M). In contrast to the behaviour of sulphides, sulphoxides are extensively protonated in this range of acid concentration. In order to take into account the extent of ionization in the different acid solutions, the fraction of protonation of methyl *p*-chlorophenyl sulphoxide was evaluated by an n.m.r. technique. This method, which has been successfully used in the case of aqueous solutions of sulphoxides,[16] is based on the variation with medium acidity of the chemical shift of the methyl group bonded to sulphur relative to that of an internal standard, Me_3N^+H, whose solvation requirements are assumed to be close to that of $\gt SOH^-$; this minimizes solvent effects. Besides changes in the fraction of protonation from 0.05 to 0.23, a change of overall acid concentration from 2.9 to 5.2M induces a 150-fold increase in reactivity. Since the sulphide concentration (4 × 10^{-3}M) is kept constant, the data of Table 2 reflect the effect of changing the acidity on k_∞ provided that the change in the extent of dissociation of HCl and its effect on the rate is negligible.

TABLE 2

First-order rate coefficients of the reaction between *p*-chlorophenyl methyl sulphoxide (5.0 × 10^{-5}M) and di-n-butyl sulphide (4.0 × 10^{-3}M) at 25 °C in MeOH–H_2O (2 : 1 v/v) in the presence of 0.98M-HCl

$[HClO_4]$/M	1.88	2.33	2.67	2.89	3.05	3.26	3.38	3.49
10^4k_{obs}/s^{-1}	0.030	0.081	0.13	0.22	0.36	0.53	0.73	0.87
10^4k/s^{-1}	0.60	1.45	1.6	2.5	3.3	4.2	5.4	5.9
f	0.05	0.056	0.082	0.087	0.11	0.127	0.135	0.147
$[HClO_4]$/M	3.61	3.73	3.88	4.04	4.14	4.24		
10^4k_{obs}/s^{-1}	1.21	1.52	2.18	2.64	3.74	4.56		
10^4k/s^{-1}	7.1	9.0	12	13	17	20		
f	0.157	0.168	0.18	0.207	0.22	0.23		

Usually the rate coefficients are corrected for the varying protonation of the substrate according to equation (3) which relates the rate coefficient for the protonated sulphoxide k to the experimental rate coefficient $k_{\mathrm{obs.}}$. Therefore k is simply $k_{\mathrm{obs.}}/f$, where f is the protonation fraction which can be calculated from the values of pK_α of the protonated sulphoxide and that of the appropriate acidity function. Since these are not available for the mixture of acids in the mixed solvents used here, we have obtained f directly from n.m.r. population measurements taking advantage of the comparable amounts of protonated and unprotonated sulphoxide present under our conditions. The correction of the rate for the protonation of the substrate is not the entire story since there is still a 35-fold increase in reactivity after this correction. This difference may be due to a further effect of acid catalysis although solvent effects cannot be entirely excluded. In the present case the possibility of correlating the rate data in terms of the Bunnett and Olsen [17] or more recent approaches [18] and their mechanistic indications are precluded. That acid catalysis occurs is substantiated only by the magnitude of the effect

$$\mathrm{rate} = k[\gt\overset{+}{\mathrm{S}}\text{–OH}] = k_{\mathrm{obs.}}[\gt \mathrm{SO}]_s \qquad (3)$$

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[16] D. Landini, G. Modena, G. Scorrano, and F. Taddei, *J. Amer. Chem. Soc.*, 1969, **91**, 6703 and references quoted therein.

[17] J. F. Bunnett and F. P. Olsen, *Canad. J. Chem.*, 1966, **44**, 1917.

[18] G. Modena, G. Scorrano, and U. Tonellato, presented at the Euchem Conference, Padova, 1975.

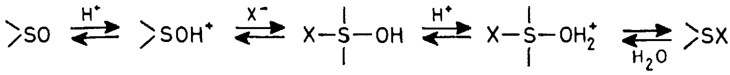
which is even greater than that observed for other halide-promoted reactions of sulphoxides such as racemization,[19, 20] reduction,[19, 20] and oxygen exchange [21, 22] which are recognized to involve the kinetic participation of a second proton. Although at present the slopes of the plot of log *k* against $-H_0$, or other acidity functions, lack any mechanistic meaning, they can however be used to compare the sensitivity of similar reactions to variations in the medium acidity. Slope values in the range 0.84—1.21 using H_0 and higher values using H_a have been reported for the racemization and reduction of the aryl methyl sulphoxides.[19] In the present case log *k* has been found to be linearly dependent on log *I* (slope 1.8; *r* 0.987), the ionization ratio of the sulphoxide ($I = [>SOH^+]/[>SO]$). This is the rate dependence on the acidity function followed by the sulphoxide under the same experimental conditions since the change in $-\log I$ describes the variations of this acidity function.

TABLE 3

Effect of the concentration of HCl on the reaction between *p*-chlorophenyl methyl sulphoxide and di-n-butyl sulphide in MeOH–H_2O (2 : 1 v/v)

[HCl] + [$HClO_4$] 4.7M, [sulphoxide]$_0$ 5 × 10^{-5}M, [sulphide]$_0$ 4 × 10^{-3}M							
[HCl]/M	0.10	0.15	0.20	0.30	0.50	0.80	1.0
$10^4 k_{obs}/s^{-1}$	0.25	0.36	0.46	0.67	1.0	1.37	1.57
[HCl] 0.7M, [$HClO_4$] 3.0M, [sulphoxide]$_0$ 5 × 10^{-6}M							
10^4[sulphide]$_0$/M	50	20	10	5.0	5.0	3.5	3.0
$10^5 k_{obs}/s^{-1}$	1.46	1.45	1.40	1.36	1.41	1.22	1.26
10^4[sulphide]$_0$/M	2.5	2.0	1.5	1.0	0.50		
$10^5 k_{obs}/s^{-1}$	1.25	1.24	1.04	0.97	0.81		
a 6.9 × 10^4 s, *b* 2.92 mol s l^{-1}, *r* 0.975							
[HCl] 0.4M, [$HClO_4$] 3.3M, [sulphoxide]$_0$ 5 × 10^{-6}M							
10^4[sulphide]$_0$/M	51.4	41.1	10	5.0	4.23	4.0	3.0
$10^6 k_{obs}/s^{-1}$ [a]	6.8	7.0	7.5	6.6	6.5	6.8	6.0
10^4[sulphide]$_0$/M	2.0	1.6	1.5	1.06	0.79	0.64	0.53
$10^6 k_{obs}/s^{-1}$ [a]	6.0	5.6	5.8	5.0	4.8	3.9	3.6
a 13.5 × 10^4 s, *b* 7.17 mol s l^{-1}, *r* 0.983							

[a] From initial rates.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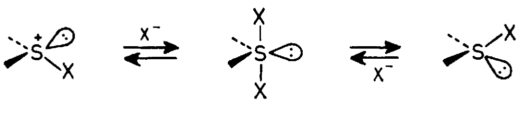
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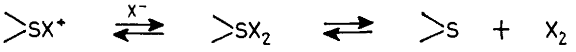
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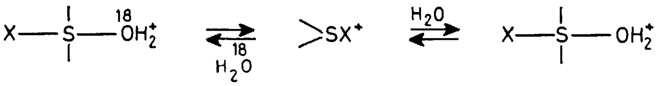
(7)

Effect of HCl.—In experiments in which the concentration of HCl was changed in the range 0.1—1.0M the total acid concentration was kept constant by addition of $HClO_4$ up to 4.7M. At least at the lowest concentration of HCl the excess of $HClO_4$ should minimize the difference in acidity of the solutions and its effect on rate. As shown from the data of Table 3 the rate increases steadily and at least in the range 0.1—0.3M, it is linearly dependent on the stoicheiometric concentration of HCl. With the reasonable assumption that the dissociation fraction of HCl in the different solutions is roughly constant, this effect should reflect first-order behaviour with respect to Cl^-. Moreover, since the experiments have been carried out in the presence of 4 × 10^{-3}M-dibutyl sulphide, the effect on $k_{obs.}$ is virtually that on k_∞, which operates in the limiting conditions when the process is zero order in sulphide. On the other hand, the effect of the concentration of HCl in the extreme situation where the rate is first order in sulphide is obtained from the comparison of the k_0 values calculated from two series of experiments carried out at constant total acid concentration [HCl] + [$HClO_4$] = 3.7M. The values of k_∞, 7 × 10^{-6} and 14.5 × 10^{-6} s^{-1}, and of k_0, 0.14 and 0.34 l mol^{-1} s^{-1} obtained in the presence of 0.4 and 0.7M-HCl, respectively, reveal similar sensitivity of both k_0 and k_∞ on changing this parameter.

DISCUSSION

The loss of water to form the halogenosulphonium cation $>SX^+$ [equation (4)] has been recognized as the rate-limiting step of halide-promoted and acid-catalysed reactions of sulphoxides which involve sulphur–oxygen bond breaking. Therefore different processes such as racemization,[19, 20, 23-26] reduction,[19, 20, 27] and oxygen exchange with water [21, 22, 26] display the same kinetic features, differing only in the fast, product-forming steps. The rapid attack of a halide ion on $>SX^+$ has been proposed to account for the racemization [equation (5; X = Cl or Br) and (6 if $>SX_2$ is an achiral dihalogenosulphurane)] and the reduction reactions (X = I) while attack of water in the reversible formation of $>SX^+$ [equation (7)]

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[19] D. Landini, G. Modena, F. Montanari, and G. Scorrano, *J. Amer. Chem. Soc.*, 1970, **92**, 7168.

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[21] I. Ookuni and A. Fry, *J. Org. Chem.*, 1971, **36**, 4097.

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[27] R. A. Strecker and K. K. Andersen, *J. Org. Chem.*, 1968, **33**, 2234.

leads to equilibration of oxygen between starting sulphoxide and the solvent.

Equation (4) apparently also accounts for the reaction between sulphoxides and sulphides in the presence of HCl since most of the kinetic features, such as first order in sulphoxide, first order in Cl^-, and second order in acid, correspond to those of the above mentioned reactions.

$$>\mathrm{SO} \xrightleftharpoons{H^+} >\mathrm{SOH}^+ \xrightleftharpoons[k_{-1}[H_2O]]{k_1 a_{H^+}[Cl^-]} >\mathrm{SCl}^+ \xrightleftharpoons[k_{-2}[>S]]{k_2[>S']} >\mathrm{S'Cl}^+ \xrightleftharpoons[k_{-3}a_{H^+}[Cl^-]]{k_3[H_2O]} >\mathrm{S'OH}^+ \xrightleftharpoons[H^+]{} >\mathrm{S'O} \qquad (8)$$

Moreover at higher sulphide concentrations the rate constant k_∞ is independent of the concentration of sulphide and equals that of racemization k_α of the sulphoxide itself. As expected, k_α is not affected by the presence of sulphide, being a measure, through the rapid scavenging by Cl^-, of the limiting rate of formation of the chlorosulphonium cation.

$$-\mathrm{d}[>SO]_s/\mathrm{d}t = \frac{k_1k_2k_3f[>SO]_s[>S'] + k_{-1}k_{-2}k_{-3}f'[>S'O]_s[>S]}{k_{-1}k_{-2}[>S] + k_{-1}k_3[H_2O] + k_2k_3[>S']}\, a_{H^+}[Cl^-] \qquad (9)$$

Thus, when $k_{obs.}$ reaches the maximum value k_∞ the sulphide apparently traps all the chlorosulphonium cation or other intermediates rapidly generated from it. On decreasing the sulphide concentration a gradual change from zero to unity in the reaction order with respect to sulphide is observed. This indicates that the rate of the step in which the sulphide is involved is so depressed that only a fraction of the intermediates is being trapped, the rest reverting to reactants through the intervention of water. With the hypothesis that $>SCl^+$ is the key intermediate in the change of oxidation state of the reactants and in agreement with the simplified reaction scheme in equation (8), where S and S′ indicate the sulphur atoms of the reactants sulphoxide and sulphide respectively and the step k_1/k_{-1} includes the steps of equation (4), all the experimental results can be accounted for. Assuming the steady state approximation for $>SCl^+$ and $>S'Cl^+$ equation (9) is the general rate expression for the pathway (8). Such a rate law, where $[SO>]_s$ and $[>S'O]_s$ indicate the total concentrations of sulphoxides, protonated or not and f and f' the corresponding protonation fractions, is simplified when a large excess of sulphide is used in the case of a reaction shifted toward products. In this case equation (9) is reduced to (10) since, besides the term for the back reaction which in each case is negligible with respect to that for the forward reaction, the term $k_{-1}k_3[H_2O] + k_2k_3[>S']_0$ is much greater than the term $k_{-1}k_{-2}[>S]$.

$$\mathrm{Rate}/[>SO]_s f = k_{obs.}/f = k = \frac{k_1k_2[>S']_0[Cl^-]a_{H^+}}{k_{-1}[H_2O] + k_2[>S']_0} \qquad (10)$$

This assumption which accords with the experimental fit to the first-order rate equation, seems justified in view of the favourable combination of both concentrations and rate constants, *i.e.* $[>S']_0 \gg [>S]$ and $k_2k_3/200$ the upper limit of $k_{-1}k_{-2}$. In fact, the equilibrium constant of 200 previously mentioned can be expressed, in terms of the rate constants of equation (8), by equation (11) and it can be safely assumed that $fk_1 \simeq f'k_{-3}$ from literature data for the iodide ion promoted reduction of alkyl aryl and dialkyl sulphoxides (*m*-chlorophenyl methyl and methyl *p*-tolyl sulphoxide react 1.4 and 2.5 times faster than DMSO in 6.8M-$HClO_4$ and the *m*-chlorophenyl methyl sulphoxide 8.2 times in 5.8M-acid [19]).

Equation (10) can be rearranged to the form of equation (2) and it accounts for the change of rate determined by the relative importance of the terms $k_{-1}[H_2O]$ and $k_2[>S']_0$, *i.e.* the relative competition for the chlorosulphonium cation by water and sulphide respectively.

$$K_e = [>S][>S'O]_s/[>S'][>SO]_s = fk_1k_2k_3/f'k_{-1}k_{-2}k_{-3} = 200 \qquad (11)$$

In the extreme situation either the concentration of sulphide is large enough to scavenge $>SCl^+$ completely to products or only a negligible fraction of the intermediate is captured, the rest reverting to reactants through the action of water; equations (12) and (13) respectively are the expressions for the specific rates.

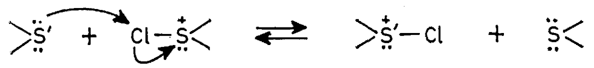
$$k_{obs.} = k_\infty = k_\alpha = fk_1[Cl^-]a_{H^+} \qquad (12)$$

$$k_{obs} = k_0[S']_0 = \frac{fk_1k_2}{k_{-1}[H_2O]}[>S']_0[Cl^-]a_{H^+} \qquad (13)$$

Combination of equations (12) and (13) gives the ratio $k_0/k_\infty = k_2/k_{-1}[H_2O]$, 4.2×10^3 l mol^{-1} in 2 : 0.75 MeOH–H_2O (4.1M-HCl) and 2.4×10^4 and 1.9×10^4 l mol^{-1} in 2 : 1 MeOH–H_2O in the presence of 0.7M-HCl–3.0M-$HClO_4$ and 0.4M-HCl–3.3M-$HClO_4$, respectively. When the correct value of the concentration of water is taken into account, these values give a measure of the relative nucleophilicity of sulphide and water towards $>SCl^+$.

Although the present results do not offer any information on the nature of the step k_2, a reasonable pathway could involve nucleophilic attack of the sulphide sulphur on the halogen atom of the chlorosulphonium cation [equation (15)]. A similar attack on the halogen atom by halide ion has been suggested as a possible route for the reduction [21] and racemization [25] of sulphoxides.

Alternative Mechanisms.—The reduction of sulphoxides by halide ion and the oxidation of sulphides by halogen can be viewed as the forward and the reverse aspect of a unified equilibrium [equations (4) and (6)] although the identity of the halogen shifts it completely in opposite directions. Moreover the existence of the species $>SX_2$ both in the pure state and in solution has been ascertained[28] and indirect evidence has been presented[29-31] for its intermediacy as the precursor of $>SX^+$ in the oxidation of sulphides by the reverse of equation (6). Thus, in principle, the change of the oxidation state of the sulphur atoms could be accounted for by other mechanistic possibilities besides step k_2 of equation (8) such as the reactions of the sulphide $>S'$ with (a) $>SX_2$ [equation (16)] or (b) the free halogen [equation (17)].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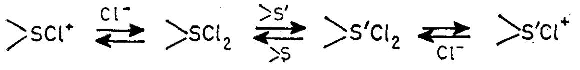
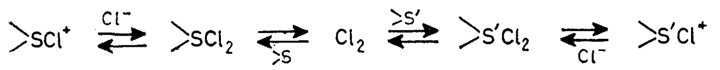

(16)

$$>SCl^+ \underset{}{\overset{Cl^-}{\rightleftarrows}} >SCl_2 \underset{>S}{\overset{>S'}{\rightleftarrows}} >S'Cl_2 \underset{Cl^-}{\rightleftarrows} >S'Cl^+$$


(17)

$$>SCl^+ \overset{Cl^-}{\rightleftarrows} >SCl_2 \underset{>S}{\rightleftarrows} Cl_2 \overset{>S'}{\rightleftarrows} >S'Cl_2 \underset{Cl^-}{\rightleftarrows} >S'Cl^+$$

Hypothesis (a) cannot be excluded in view of the favourable equilibrium of formation of $>SCl_2$ starting from sulphide as well as from the halogenosulphonium intermediate. Thus a value of 5×10^5 l mol^{-1} for the equilibrium constant of the formation of $>SCl_2$ has been reported for the reaction between chlorine and bis-(*p*-chlorophenyl) sulphide[32] in CH_2Cl_2 and CH_3CN together with a lack of evidence for appreciable concentration of a chlorosulphonium intermediate. The formation of $>SCl_2$ starting from $>SCl^+$ should also be kinetically favoured in view of the large halide–water competition factor found for iodo- and bromo-sulphonium intermediates.[29,31]

Distinction among these possibilities is difficult since the routes described by equations (15)—(17) are involved at the borderline region of the rate-determining step. However the dependence of k_0 on the concentration of HCl could be used as a diagnostic criterion since, at variance with path (15) *via* $>SCl^+$, the other routes imply the kinetic participation of a second chloride ion during or before the step in which sulphide $>S'$ is involved. With respect to k_0 comparison of the ratios $k_0 : k_\infty$ obtained at different HCl concentrations offers the chance of ignoring the effects of acid catalysis.* This comparison indicates the route *via* $>SCl^+$ as the most likely path. However contributions by other routes cannot be excluded. Uncertainties arising from experimental difficulties in carrying out measurements at lower concentration of sulphide $>S'$ and acid do not allow the determination of $k_{obs.}$ values which differ greatly from k_∞ and, therefore, the calculation of more accurate values for k_0 or k_0/k_∞. The range of concentrations of HCl which should be explored for a correct order determination with respect to Cl^-, does not allow for changes in the extent of dissociation of HCl and medium effects on the $k_0 : k_\infty$ ratio, including those arising from changes in water activity. Moreover some considerations seem to rule out the path *via* Cl_2 leaving only $>SCl_2$ as a possible competitor with SCl^+ for the sulphide $>S'$. Indeed, if in addition to the steady-state conditions for $>SCl^+$, $>SCl_2$, Cl_2, $>S'Cl_2$, and $>S'Cl^+$ and to the approximations used for the calculation of equation (10), the chlorosulphonium intermediates are assumed to react with Cl^- faster than with water and Cl_2 with dialkyl sulphides faster than with alkyl aryl sulphides,† the rate law calculated for equation (17) does not involve the variable reaction order observed in the sulphide S′. On the contrary, as appears from the rate law calculated on the base of the above assumptions, the route described by equation (16) accounts for this effect.

EXPERIMENTAL

Reagent grade di-n-butyl sulphide, methyl phenyl sulphide, and di-n-butyl sulphoxide were repeatedly distilled and their purity checked by g.l.c. The syntheses of (±)-[34] and (+)-*R*-methyl *p*-chlorophenyl sulphoxide (Ia)[35] and of methyl phenyl sulphoxide (Ic),[34] methyl *p*-tolyl sulphoxide (Ib),[34] methyl *p*-chlorophenyl sulphide (IIIa),[36] and methyl *p*-tolyl sulphide (IIIb)[37] have been described.

Reaction between Aryl Methyl Sulphoxides and Sulphides.—A solution of the reactants (0.01—0.03M) in the appropriate solvent containing 4M-HCl was allowed to react at 25° and samples were periodically analysed by g.l.c. to determine the amount of sulphide present. The following procedure was used. The reaction solution (10 ml) was quenched by addition of water (25 ml) and benzene (10 ml) containing a hydrocarbon (dodecane, tridecane, or tetra-

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* Acid catalysis should not affect this ratio as it is common to both k_0 and k_∞.

† PhSPr was found to react with Br_2 at least 100 times slower than Pr_2S.[33]

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decane) as internal standard. The organic layer was extracted with water (4 × 20 ml), dried (Na_2SO_4), and injected into an aerograph model 1520 g.l.c. instrument with a 5 ft × 1/4 in column of 5% SE 30 on Chromosorb W at 150—165 °C. The calibrations factors of sulphide using the internal standards were determined following the same experimental procedure. In the case of the reaction between (Ic) (0.031M) and (IIIb) (0.0306M) in 2 : 0.75 MeOH–H_2O (an equilibrium reaction) analysis gave:

10^2[PhSMe]/M	0.08	1.25	1.81	1.82
10^2[*p*-tolylSMe]/M	3.06	1.82	1.22	1.21
t/min	2	65	250	570

Similar good balances of products were also obtained in other cases. Identification of products was achieved by co-injection with authentic samples. Analysis of the sulphoxides required several extractions of the reaction mixture with chloroform followed by g.l.c. analysis on a Carbowax 20 M TPA column.

Kinetic Measurements.—The reaction was followed spectrophotometrically by recording the increase in optical density at 258 nm on a Gilford model 2400 instrument and the value of $k_{obs.}$ in most cases was calculated according to the Guggenhein method for the first-order rate equation. For slower runs $k_{obs.}$ was obtained from the initial rates. Polarimetric experiments were followed on a Perkin-Elmer model 141 instrument at 365 nm.

Protonation of p-*Chlorophenyl Methyl Sulphoxide*.—N.m.r. spectra were recorded on a 90 MHz Brucker HFX 10 instrument for solutions in 2 : 1 [$^2H_3$]methanol–water containing 0.98M-HCl, 0—4.2M-$HClO_4$, and trimethylammonium chloride as internal standard. The protonation fractions reported in Table 2 were calculated according to equation (18) where $\Delta\nu$, $\Delta\nu_{,BH^+}$ and $\Delta\nu_B$ are the chemical shifts of the methyl group of the partially protonated, fully protonated, and free base sulphoxide, respectively referred to that of the internal standard (d, *J* 5 Hz). The $\Delta\nu_{BH^+}$ value (δ 43.5) was measured in 13.5M-H_2SO_4 and the value δ −5.5, measured in the presence of 0.4M-HCl, was taken as that of $\Delta\nu_B$ in order to minimize some uncertainty which affects this value. Indeed $\Delta\nu$ decreases slowly on decreasing the acid concentration below 0.5M, a region in which a change in the extent of protonation should not occur since alkyl aryl sulphoxides in water are virtually un-ionized [16] and, low concentrations of acid being equal, the aqueous–organic media are less acidic than the aqueous solutions.* For this reason solvent effects provide a better explanation, $\Delta\nu$ being the difference of chemical shifts of a neutral and a charged species which is affected differently by the change (acid addition) in the solvent composition.

$$f = [BH^+]/([BH^+] + [B]) = (\Delta\nu - \Delta\nu_B)/(\Delta\nu_{BH^+} - \Delta\nu_B) \quad (18)$$

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* The values of H_0 for 0.5M-acid solutions in water are 0.12 [38] (H_2SO_4) and 0.20 [38] (HCl) but 1.42 [39] ($HClO_4$), 1.76 [40] (H_2SO_4), and 2.0 [40] (HCl) in 60 : 40 dioxan–water and 1.1 [40] (H_2SO_4) and 1.18 [40] (HCl) in 40 : 60 dioxan–water.

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