Oxygen Exchange between Sulphoxides and Sulphides. Part 3.[1b] The HCl-Catalysed Reduction of Aryl Methyl Sulphoxides by Dialkyl Sulphides in Aqueous Methanol

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Dialkyl sulphides reduce aryl methyl sulphoxides in aqueous methanol in the presence of *ca.* 4 mol dm^{-3} HCl. Ring substitution in phenyl methyl sulphoxides moderately affects their reactivity towards dibutyl sulphide, the overall effect resulting in a Hammett ρ value of -1.6. This parameter is a measure of the effect of structural changes on a protonation pre-equilibrium, the formation of chlorosulphonium ion, and its subsequent partitioning between reduction and return to reactants by the action of water. Changing the alkyl moiety of the sulphides induces moderate reactivity changes suggesting a compensation of opposite polar and steric effects. Sulphoxides with electron-releasing groups display the highest selectivity towards dialkyl sulphides. When a large concentration of sulphide is used, both racemization of chiral sulphoxide and ^{18}O exchange with the aqueous solvent are suppressed and this suggests that the species ArR^{1}SCl$^+$ is a common intermediate for these processes and for the reduction reaction. These and other kinetic findings indicate that the reduction step involves the displacement at the ArR^{1}SCl$^+$ chlorine of a sulphide by a sulphide molecule rather than by chloride ion and rules out, for the racemization too, the hypothesis involving a free halogen intermediate.

It has been suggested[1a] that the HCl-catalysed oxygen transfer between sulphoxides and organic sulphides, eqn. (1), occurs in aqueous media *via* a direct chloronium ion transfer from a chlorosulphonium intermediate, eqn. (2).

$$\mathrm{ArSOR^1 + R^2K^3S \xrightleftharpoons[\text{aq. MeOH}]{\text{HCl}} ArSR^1 + R^2R^3SO} \qquad (1)$$

$$\mathrm{R^1, R^2 = alkyl;\ R^3 = alkyl, aryl}$$

$$\mathrm{ArR^1S^+{-}Cl + SR^2R^3 \xrightleftharpoons[k_{-2}]{k_2} ArR^1S + Cl{-}S^+R^2R^3} \qquad (2)$$

In contrast, results obtained in non-hydroxylic media indicate that free chlorine is the intermediate responsible for the equilibration of the oxidation states of the sulphur atoms,[2] eqn. (3). In this connection, the alternative fate of ArR^{1}SCl$^+$

$$\mathrm{ArR^1S^+{-}Cl \xrightleftharpoons[k'_{-2}[ArR^1S]]{k'_2[Cl^-]} Cl_2 \xrightleftharpoons[Cl]{k'_3[R^2R^3S]} R^2R^3S^+{-}Cl} \qquad (3)$$

with either Cl$^-$ or R^{2}R^{3}S has been rationalized in terms of solvation effects.[2a] Thus in water, alkyl sulphides are expected to be better nucleophiles than Cl$^-$ towards the chlorine atom of a chlorosulphonium ion, while the opposite is true in non-protic media where Cl$^-$ is less solvated. However, free chlorine has been detected as a product of the reaction of a particular sulphoxide in aqueous HCl.[3] Moreover, diaryl sulphoxides undergo deoxidation that is often coupled with reductive chlorination both in aqueous and non-aqueous solutions of HCl.[4] This would imply that the free chlorine mechanism may also be involved in the oxygen transfer from sulphoxide to sulphide in aqueous solvent. To provide a more definite solution of this problem, the present study reports the kinetic investigation of the HCl-catalysed reaction between aryl methyl sulphoxides, $>$SO, and some dialkyl sulphides, $>$S$'$, in aqueous methanol.

Results

Kinetics.—Although we are discussing reversible processes, in practice all reactions proceeded virtually to completion since the equilibria are largely in favour of the products. Typically the equilibrium constants for dibutyl sulphide are 500 in the reaction with methyl *p*-tolyl sulphoxide and 2700 for the reaction with methyl *p*-chlorophenyl sulphoxide.[5] Moreover, an excess of sulphide, $[>S']_0/[>SO]_0 = 8$–50, ensured both completion of reaction and pseudo first-order conditions. For each set of experiments, Tables 1–3 report the upper and lower limits but not the individual values observed for the first-order rate coefficient, k_{obs}, over the range of reactant concentrations explored. For each pair of sulphoxide–sulphide reaction investigated, k_{obs} does not change on changing $[>SO]_0$ but depends instead on the initial concentrations of sulphide $[>S']_0$ and follows, in all cases, the asymptotic trend previously observed.[1a] The rate increases almost linearly at the lowest concentrations and then levels off to a plateau region at which both the concentration and the nature of sulphide become unimportant. The rate coefficients, k_0 and k_∞, for the extreme situations in which the reaction is zero- and first-order with respect to sulphide, were calculated according to the empirical eqn. (4).

$$k_{obs}^{-1} = k_\infty^{-1} + \{k_0[>S']_0\}^{-1} \qquad (4)$$

Structural Effects.—The ρ values for the phenyl ring substitution (using σ parameters) are -1.6 ± 0.1 (r 0.993) in the case of k_0 and -0.95 ± 0.15 for k_∞; in the latter case, the poor correlation (r 0.97) is mainly due to the *p*-methoxy derivative. At any rate, the ρ value is close to that (-0.72, r 0.98) reported by Landini *et al.*[6] for a wider set of substituents for the reduction of the same substrates by HI in water. The rate values from the authors cited correlated well with the corresponding k_∞ constants ($\log k_\infty$ *vs.* $\log k_{HI}$, r 0.997, slope 1.12).

The polar effect due to the protonation of the sulphoxides can

Table 1 Values of k_0 and k_∞ for the reaction between ring X-substituted methyl phenyl sulphoxides and dibutyl sulphide at 25.0 °C in MeOH–H_2O (2:0.75, v/v) in the presence of 4.2 ± 0.1 mol dm^{-3} HCl

[HCl]/ mol dm^{-3}	Substituent X	[sulphoxide]$_0$/ 10^{-5} mol $dm^{-3\,a}$	[sulphide]$_0$/ 10^{-5} mol $dm^{-3\,a}$	n^b	r^b	$k_{obs}/10^{-4}\ s^{-1\,c}$	$k_\infty/10^{-4}\ s^{-1}$	k_0/dm^3 mol^{-1} s^{-1}	$(k_0/k_\infty)/10^3$ dm^3 mol^{-1}	f
4.225	4-MeO	0.9–9.1	8.04–804	15	0.997	1.5–2.83	2.86 ± 0.03	3.32 ± 0.07	11.6	0.23
4.24	4-Me	0.5–5	5–205	20	0.995	1.04–3.25	3.11 ± 0.14	3.04 ± 0.15	9.8	0.18
4.13	4-Me	0.5	2.3–480	20	0.993	0.4–2.6	2.44 ± 0.14^d	2.12 ± 0.1	8.7	—
3.93	4-Me	5–8	10–300	17	0.991	0.7–1.5	1.55 ± 0.1^e	1.29 ± 0.1	8.3	—
4.23	H	0.6–9.1	6.14–614	15	0.999	0.60–2.33	2.36 ± 0.04	1.30 ± 0.02	5.5	0.14
4.22	4-Cl	0.5–5	5.05–505	18	0.991	0.23–1.20	1.20 ± 0.1	0.50 ± 0.02	4.9	0.11
4.225	3-Cl	0.53–8	6.1–509	21	0.988	0.21–0.87	0.77 ± 0.05	0.37 ± 0.02	4.8	0.092

^{a} Concentration range explored. ^{b} Number of experiments and correlation coefficient of k_{obs}^{-1} *vs.* [sulphide]$_0^{-1}$. ^{c} Observed range of rates. ^{d} For [(+)-(*R*)-sulphoxide]$_0$ = 5×10^{-3} mol dm^{-3} alone: $k_\alpha = 2.45 \times 10^{-4}\ s^{-1}$ and $k_\alpha = 2.55 \times 10^{-4}\ s^{-1}$ in the presence of 5×10^{-3} mol dm^{-3} Bu_2S. ^{e} For [(+)-(*R*)-sulphoxide]$_0$ = 5.2×10^{-2} mol dm^{-3} alone: $k_\alpha = 1.60 \times 10^{-4}\ s^{-1}$ and $k_\alpha = 1.65 \times 10^{-4}\ s^{-1}$ in the presence of 3×10^{-3} Bu_2S.

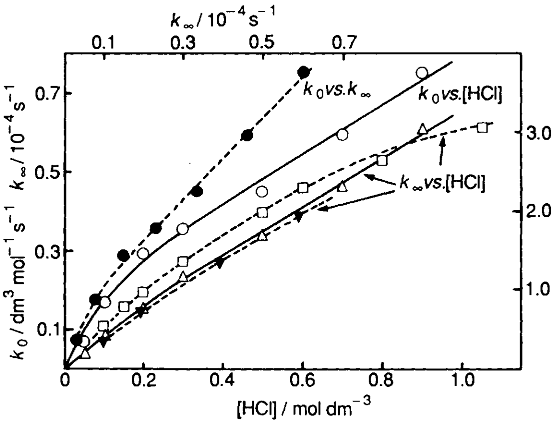


Fig. 1 Effect of [HCl] on k_∞ and k_0 for the reaction of methyl *p*-tolyl sulphoxide with dialkyl sulphides in MeOH–H_2O (2:1, v/v) at 25 °C. Left hand ordinate: 1,4-oxathiane (——), k_∞ (△) and k_0 (○), [HCl] + [$HClO_4$] = 4.0 mol dm^{-1}; plot of k_0 *vs.* k_∞ (- - - - ●); Bu_2S (— — —), k_∞ (▼), [HCl] + [$HClO_4$] = 3.9 mol dm^{-3}. Right hand ordinate: Bu_2S (- - - -), k_∞ (□), [HCl] + [$HClO_4$] = 4.7 mol dm^{-3}

be evaluated from their protonation fraction, *f*, as determined by ^1H NMR spectroscopy;[7] $f = [{>}SOH^+]/[{>}SO]_s$, where $[{>}SO]_s$ is the stoichiometric concentration of sulphoxide, and is also reported in Table 1. The reactivity of the protonated sulphoxide, *k*, is related to the experimental rate coefficient in acidic solutions, k_{obs}, by eqn. (5).[8] As a consequence the

$$\text{rate} = k_{obs}[{>}SO]_s = k[{>}SOH^+] \qquad (5)$$

ρ values related to the k_∞ and k_0 constants include a value of −0.56 (the slope of log f *vs.* σ, *r* 0.983), which accounts for the different extent of protonation of the various sulphoxides. In terms of basicity, as measured by their pK_a values, the estimate ρ = 0.69 ± 0.07 (from the slope of $-\log[{>}SOH^+]/[{>}SO]$ *vs.* σ, *r* 0.984), approaches that reported for aqueous solutions (0.85).[7]

Changes in the alkyl moiety of the dialkyl sulphides resulted in the data given in Table 2. Open chain and cyclic sulphides reacting with methyl *p*-tolyl and methyl *p*-chlorophenyl sulphoxide gave, within experimental error, the same k_∞ value for all sulphides reacting with the same sulphoxide. On the contrary, a moderate spread of k_0 values was observed depending on the nature of both the sulphoxide and the sulphide considered.

Effect of HCl.—The measurements were performed in the presence of a large acid buffer, $HClO_4$, partly replaced by variable amounts of HCl so as to explore a still moderate but significant range of concentrations. This minimizes the effects due to possible changes in the acidity of the solutions. Indeed, molarity being equal, solutions > 2 mol dm^{-3} $HClO_4$ in water[9a] and in mixed solvents[9b] appear somewhat more acidic (as measured by H_0) in comparison to HCl solutions and they display lower water activity.[10] It follows that the more the common ion H^+ activity and, hence, the dissociation fraction of HCl remain constant, the more a_{Cl^-} should be proportional to stoichiometric HCl, and the observed reactivity should therefore be as a result of changes in a_{Cl^-}.

The replacement of some $HClO_4$ with HCl (from 0.05–0.9 mol dm^{-3}; 4 mol dm^{-3} total acid, Table 3) is not relevant as far as the protonation of methyl *p*-tolyl sulphoxide is concerned since *f* does not change. Plots of k_∞ *vs.* [HCl], while approaching a linear correlation, show a slightly downward curvature (Fig. 1). This trend is more pronounced in more acidic solutions and does not depend on the sulphoxide. Thus, when [HCl] + [$HClO_4$] = 4.7 mol dm^{-1} (here $k_{obs} \approx k_\infty$), methyl *p*-chlorophenyl-[1a] and methyl *p*-tolyl sulphoxide (see Fig. 1), reacting with Bu_2S (4.0×10^{-3} mol dm^{-3}) gave constant reactivity ratios ($k_{p\text{-Me}}$ *vs.* $k_{p\text{-Cl}}$ slope 1.93, *r* 0.992, eight experiments) in the range [HCl] = 0.1–1.0 mol dm^{-3}. Experiments carried out with methyl *p*-tolyl sulphoxide reacting with Bu_2S and 1,4-oxathiane at lower acid concentration ([HCl] + [$HClO_4$] = 3.9 and 4.0 mol dm^{-3}, respectively) gave (see Fig. 1) plots of k_∞ *vs.* [HCl] which are much closer to linearity. As a consequence, first-order kinetics with respect to Cl^- can be safely assumed in the case of k_∞.

The plots of k_0 and k_∞ *vs.* [HCl], obtained simultaneously for 1,4-oxathiane, are not superimposable, although the trends are similar. Assuming that the dependence on Cl^-, acid catalysis, and any other effect connected with the HCl–$HClO_4$ composition are the same for both parameters, the ratio k_0/k_∞ should be constant and the plot of k_0 *vs.* k_∞ should give a straight line. The downward curvature still evident appears to be related to changes of k_0/k_∞ (Table 3) by a factor of 1.7 in the range 0.05–0.9 mol dm^{-3} HCl. Nevertheless, the first-order rate dependence on Cl^- is also assumed for k_0, and the discrepancy is likely also to be a consequence of another relevant kinetic parameter included therein. This is expected from the mechanism previously proposed,[1a] according to which water is a kinetically active species [step k_{-1}, eqn. (6)] and its activity may change, although not dramatically, by replacing HCl with $HClO_4$.

The operation of acid catalysis has the same effect on both k_0 and k_∞. Although the individual values change appreciably, k_0/k_∞ remains virtually constant in experiments performed on methyl *p*-tolyl sulphoxide without acidity compensation in the presence of 3.93–4.24 mol dm^{-3} HCl (Table 1) and of 0.1 mol dm^{-3} HCl with 3.8 and 3.9 mol dm^{-3} $HClO_4$ (Table 3). Under these conditions changes in the H^+ activity are kinetically much more effective than those of Cl^- or H_2O.

Table 2 Values of k_0 and k_∞ for the reaction between aryl methyl sulphoxides and dialkyl sulphides, R^2R^3S, at 25.0 °C in $MeOH-H_2O$ (2:0.75, v/v) in the presence of 4.2 ± 0.1 mol dm^{-3} HCl

	R^2, R^3							
(*a*) *p*-MeC_6H_4-SOMe[a]	Me, Me	Bu^n, Bu^n	Pr^i, Pr^i	Bu^s, Bu^s	3-Pentyl, 3-Pentyl	$(H_2C)_2\!<\!{CH_2-\atop CH_2-}$	$(H_2C)_3\!<\!{CH_2-\atop CH_2-}$	$O\!<\!{CH_2CH_2-\atop CH_2CH_2-}$
[HCl]/mol dm^{-3}	4.25	4.24	4.25	4.25	4.225	4.18	4.18	4.15
[sulphide]$_0$/10^{-5} mol dm^{-3} [b]	5.7–575	details in Table 1	5–500	5.1–513	5–500	3.3–540	2.3–470	6.6–1040
n[c]	16 0.996		12 0.995	15 0.993	20 0.998	20 0.998	15 0.999	18 0.998
k_{obs}/10^{-4} s^{-1} [d]	0.95–2.92		0.90–3.0	0.72–3.0	0.39–2.72	0.70–2.44	0.47–2.40	0.22–2.30
k_∞/10^{-4} s^{-1}	3.03 ± 0.16	3.11	3.12 ± 0.19	3.03 ± 0.11	2.90 ± 0.19	2.45 ± 0.06	2.38 ± 0.05	2.30 ± 0.15
k_0/dm^3 mol^{-1} s^{-1}	2.38 ± 0.11	3.04	2.54 ± 0.13	1.85 ± 0.03	0.91 ± 0.02	3.1 ± 0.06	2.46 ± 0.02	0.34 ± 0.02
(k_0/k_∞)/10^3 dm^3 mol^{-1}	7.8	9.8	8.1	6.1	3.1	12.6	10.4	1.5

	R^2, R^3			
(*b*) *p*-ClC_6H_4SOMe[a]	Bu^n, Bu^n	Pr^i, Pr^i	Bu^s, Bu^s	3-Pentyl, 3-Pentyl
[HCl]/mol dm^{-3}	4.22	4.22	4.23	4.225
[sulphide]$_0$/10^{-5} mol dm^{-3} [b]	details in Table 1	3.0–201	5.0–500	5.5–505
n[c]		18 0.995	14 0.997	20 0.985
k_{obs}/10^{-4} s^{-1} [d]		0.16–1.30	0.21–1.16	0.17–1.18
k_∞/10^{-4} s^{-1}	1.20	1.20 ± 0.17	1.20 ± 0.11	1.20 ± 0.1
k_0/dm^3 mol^{-1} s^{-1}	0.59	0.56 ± 0.03	0.49 ± 0.02	0.38 ± 0.03
(k_0/k_∞)/10^3 dm^3 mol^{-1}	4.9	4.7	4.1	3.2

[a] Initial concentrations (0.5–5) × 10^{-5} mol dm^{-3}. [b] Concentration range explored. [c] Number of experiments and correlation coefficient of k_{obs}^{-1} *vs.* [sulphide]$_0^{-1}$. [d] Observed range of rates.

Table 3 Effect of the concentration of HCl on the values of k_0 and k_∞ for the reaction between methyl *p*-tolyl sulphoxide[a] and 1,4-oxathiane at 25.0 °C in $MeOH-H_2O$ (2:1, v/v) in the presence of acid, [HCl] + [$HClO_4$] = 4.0 mol dm^{-3}

[HCl]/mol dm^{-3}	[$HClO_4$]/mol dm^{-3}	[sulphide]$_0$/10^{-5} mol dm^{-3} [c]	n[d]	r[d]	k_{obs}/10^{-5} s^{-1} [e]	k_∞/10^{-5} s^{-1}	k_0/10^{-2} dm^3 mol^{-1} s^{-1}	(k_0/k_∞)/10^4 dm^3 mol^{-1}	f
0.05	3.95	5.3–1050	15	0.990	0.18–0.35	0.35±0.07	6.4±0.3	1.8 ± 0.4	0.19
0.10	3.90	5.1–1020	14	0.993	0.48–0.79	0.79±0.05	16.8±2	2.1 ± 0.3	0.17
0.10	3.80	5.4–1070	19	0.997	0.32–0.65	0.65±0.07	11±1	1.7 ± 0.2	—
0.20	3.80	5,3–1050	18	0.998	0.81–1.50	1.48±0.05	30±1	2.0 ± 0.1	0.18
0.30	3.70	5.2–1040	15	0.992	1.1–2.4	2.3±0.05	36±1.3	1.6 ± 0.07	0.17
0.50	3.50	5.2–1040	15	0.994	1.4–3.4	3.34±0.1	45±2	1.35 ± 0.07	0.19
0.7	3.3	5.5–1050	14	0.995	1.8–4.4	4.6±0.08	59±2	1.28 ± 0.05	0.19
0.9[b]	3.1	5.1–1030	19	0.997	2.0–6.2	6.0±0.15	75±3	1.24 ± 0.06	0.17

[a] Initial concentration 5.5 × 10^{-5} mol dm^{-3}. [b] [sulphoxide]$_0$ = (0.55 – 5.5) × 10^{-5} mol dm^{-3}. [c] Concentration range explored. [d] Number of experiments and correlation coefficient. [e] Observed range of rates.

Racemization and ^{18}*O Exchange Experiments.*—In the case of both (+)-(*R*)-methyl *p*-chlorophenyl sulphoxide[1a] and (+)-(*R*)-methyl *p*-tolyl sulphoxide (see footnote *d* of Table 1) the loss of optical activity, k_α, equals k_∞ and the addition of Bu_2S does not affect k_α but promotes the rate of reduction, k_{obs}.

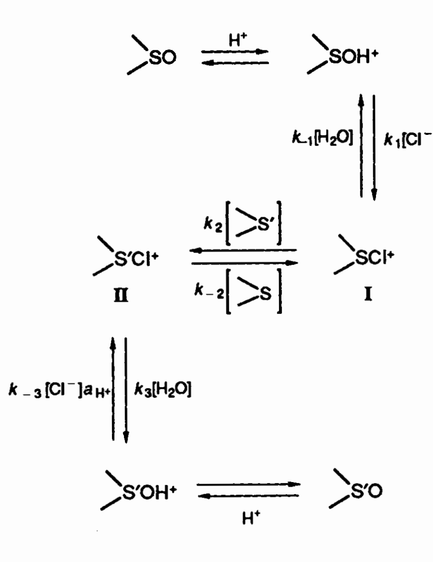
On the contrary, sulphide, when present in sufficiently large amounts so that $k_{obs} = k_\infty$, quenches both racemization and ^{18}O exchange. A sample of 15.9% ^{18}O-enriched methyl *p*-tolyl sulphoxide was allowed to proceed approximately to half reaction. Upon isolation, 9.1% ^{18}O atoms were still present, *ca.* 50% of the initial content. The experiment was repeated in the presence of 3.6 × 10^{-2} mol dm^{-3} Me_2S, a concentration at which the reduction reaction reaches the maximum rate: the unreacted sulphoxide then contained 15.1% ^{18}O atoms, *i.e.* its initial content within experimental error.

Under similar conditions, (+)-(*R*)-methyl *p*-tolyl sulphoxide, both in the absence and in the presence of 3.6 × 10^{-2} mol dm^{-3} Me_2S, retained (after the same reaction time) 42.1% and at least 95.6% of the original chirality, respectively.

Discussions

On the whole, the mechanistic route previously suggested[1a] for the reduction of *p*-chlorophenyl methyl sulphoxide by dibutyl sulphide, eqn. (6), accounts for all the features of the HCl-catalysed reductions in aqueous media.

Eqn. (7) relates, under pseudo first-order conditions, rates and [$>S'$]$_0$ to the elemental steps of eqn. (6). It is derived from the general rate equation, assuming[1a] that the term related to the back reaction is negligible and that $k_{-1}k_{-2}$ [$>S$] $\ll$ $k_{-1}k_3$ [H_2O] + k_2k_3[$>S'$]$_0$. This is quite reasonable, even in the least favourable case of methyl *p*-methoxyphenyl sulphoxide (for which $K_e \approx 300$, determined by extrapolation of the relevant values for the *p*-methyl- and *p*-chloro-compounds),



(6)

in view both of the large equilibrium constant and the absence of any evidence of mass law effect by $>S$.

$$\text{Rate}/f[>SO]_s = k_{obs}/f = \frac{k_1k_2[>S']_0[Cl^-]a_{H^+}}{k_{-1}[H_2O] + k_2[>S']_0} \quad (7)$$

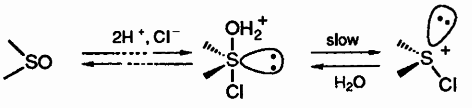
The rate-limiting step pivots around species **I**. Its formation, step k_1, is the slow step of the reduction when $[>S']$ is sufficiently large that $k_2[>S']_0 \gg k_{-1}[H_2O]$, and under such conditions any **I** formed is converted into $>S$, and k_{obs} then reaches the maximum value, k_∞. In the opposite case the back reaction with water reverts most of **I** to sulphoxide and the subsequent step becomes rate-limiting. Eqns. (8) and (9) can be

$$k_{obs} = k_\infty = k_\alpha = fk_1[Cl^-]a_{H^+} \quad (8)$$

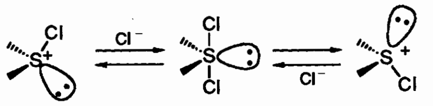
$$k_{obs} = k_\infty k_2[>S']_0/k_{-1}[H_2O] = k_0[>S']_0 \quad (9)$$

derived for these two extreme situations. In particular these agree with the acid catalysis which affects k_0 and k_∞ in the same way, with both displaying first-order dependence on $[Cl^-]$. However, in view of its first-order dependence on $>S'$, k_0 provides information on the step, beyond the formation of the chlorosulphonium **I**, in which the sulphur atoms balance their oxidation states. So any alternative mechanism which implicates two chloride ions, either during or before the step involving $>S'$, and intermediates such as Cl_2 or $>SCl_2$, appears quite unlikely for the reduction reaction.

The results of stereochemical and ^{18}O-tracer experiments also support these mechanistic conclusions. The rate-determining formation of chlorosulphonium ion **I**, eqn. (10), has been suggested in order to explain the similar, if not identical, kinetic behaviour shown by different chloride- and acid-promoted[11,12] reactions such as reduction,[6,8,13] racemization[6,8,14] and oxygen exchange,[14b–d,15] the details of their product-forming stages remaining a debatable question. So the scheme of eqn. (3) accounts for the chloride-induced racemization; however, the equilibrium shifted to the left can not produce sizeable amounts of sulphide in the absence of an external reducing reagent. Arguments in favour of this pathway have been obtained in water[16] only for an atypical sulphoxide, and in non-aqueous media for both racemization and reduction of cleavable[2c] and non-cleavable[2a,b] sulphoxides. In the latter case, racemization and reduction occur at the same rate and both are second-order with respect to Cl^- and zero-order with respect to $>S'$. Alternatively, racemization could occur through inversion of configuration of **I** [eqn. (11)] involving $>SCl_2$ either as an intermediate or a transition state.[15b]



I (10)



(11)

Racemization and ^{18}O-exchange occur in water at the same rate[14b,15] and this has been explained by invoking the same intermediate **I** which, once slowly and reversibly formed, undergoes fast racemization. If reduction by $>S'$ follows eqn. (6) and the reaction in eqn. (11) is the only process accounting for racemization, then the rate of the latter, k_α, will be the upper limit for reduction and can not be affected by $>S'$. In this case, when **I** is completely scavenged towards reduction by high concentrations of $>S'$, neither racemization nor ^{18}O-exchange should be detected in the starting material isolated before reaction is complete. In the absence of $>S'$, the same degree of exchange and racemization is expected; this agrees exactly with our findings.

On the contrary, the present findings do not agree with the reaction scheme of the combined eqns. (10) and (3), as previously proposed[2] for racemization and oxygen-transfer reactions in non-aqueous media. Accordingly, racemization and ^{18}O-exchange should again occur in the absence of external sulphide $>S'$ but, depending on $[Cl^-]$, their rates could differ considerably thus leading to different extents of exchange and racemization in the unreacted material. Moreover, since exchange and racemization take place on different intermediates, if R^2R^3S (assumed to be unable to scavenge ArR^1SCl^+ in aqueous media too) competes effectively with ArR^1S for Cl_2, *i.e.* in eqn. (3) $k'_3[R^2R^3S] \gg k'_{-2}[ArR^1S]$, then racemization but not ^{18}O-exchange will be suppressed by R^2R^3S. In other words, at high Me_2S concentrations, racemic species should be diverted from the starting chiral sulphoxide, but the ^{18}O label should always be lost.

Racemization according to eqn. (3), coupled with reduction as outlined in eqn. (6) appears to be quite unrealistic: in order to maintain the kinetic features found for k_0, $>S'$ (as compared with $>S$) could not trap Cl_2 while reacting with $>SCl^+$.

The reaction is zero-order with respect to $>S'$, and k_∞ (Table 2) is the same for the same sulphoxide and different sulphides under the same conditions. That k_∞ measures the rate up to the step k_1 is also supported by the ρ value. This is close, even for its component related to the protonation pre-equilibrium, to that found for the racemization by Cl^- and Br^- and the reduction by I^- of phenyl methyl sulphoxides in water.[6]

By analogy with the halogenation and oxidation reactions by Hal–O– and Hal–N= species, step k_2 of eqn. (6) is claimed[1a] to involve the displacement of sulphide $>S$ by $>S'$ on the halogen atom of $>SCl^+$. In common with other heterosulphonium compounds,[17] halosulphonium displays electrophilic reactivity on both sulphur and the heteroatom, the latter towards a variety of substrates.[2,6,15b,16,18] Substituent effects on the sulphoxide provides no important information concerning the nature of step k_2 since $k_2 = k_0k_{-1}[H_2O]/k_\infty$ [eqn. (9)] and the present results do not allow us to evaluate the contribution of the term k_{-1}. When the substituent effects on k_∞ and k_0 are taken into account, the ratio k_0/k_∞, a measure of the relative nucleophilicity ratio of $>S'$ and water for **I**, increases with the electron-releasing capability of **I** ($\rho = -0.6$ to -0.8). This is against the expected effect for both k_2 and k_{-1} and can be tentatively explained in terms of a favourable electron-withdrawing effect on both, the last being larger than the first.

On the contrary, structural changes on $>S'$ are expected to induce changes of k_0 and k_0/k_∞ which, for a given sulphoxide, would reflect the effect on k_2 alone. Although the approach to sulphur may be retarded for steric reasons, halonium transfer to sulphide from halogenating species often shows large polar effects.[19] Their importance stems in the present case from the comparison between thiane and 1,4-oxathiane which reacts 10 times slower, although the protonation of oxygen is very slight if it takes place at all: the ^{1}H NMR chemical shift of $O–CH_2–$[20] does not change in the presence of 4 mol dm^{-3} $HClO_4$ in aqueous methanol.

The relative reactivities of the cyclic sulphides thiolane and thiane also indicate k_2 to be the rate-determining step. In fact, since the addition of a ligand induces only small changes in the geometry around sulphur, the reactivity of cyclic substrates is expected to be little sensitive to ring size but enhanced relative to the open-chain sulphides. The ratio of the five- to the six-membered derivatives observed here (1.2) is in agreement with expectation (nucleophilic approach to the trivalent sulphur involves, by contrast, its rehybridization and ratios of 50–400[21,11]) and is close to the values of 0.8 and 1.2 reported for the reaction with Bromamine T[19e] and Chloramine T,[19d] both of which involve a rate-determining halonium transfer, and for other oxidations of sulphur. Based on this evidence and on the lack of mass-law phenomena by $>S$, the kinetic involvement of step k_3 seems unlikely.

Structural changes on open-chain dialkyl sulphides reveal for k_0 a balance of polar and steric effects resulting in a low selectivity which appears to be between that displayed by the same sulphides in the reaction with Chloramine T and Bromamine T, and somewhat similar to that reported for the oxidation by bromine of phenyl alkyl sulphides having the same alkyl structure.[19b] The spread of rates observed for different sulphides depends on the nature of the reacting sulphoxide. It is broader for methyl *p*-tolyl than for methyl *p*-chlorophenyl sulphoxide (Me:Bu^n:Pr^i:Bu^s:3-pentyl, 0.78:1:0.83:0.61:0.3 and Bu^n:Pr^i:Bu^s:3-pentyl, 1:0.95:0.83:0.64) but the correlation observed ($[\log k_0/k_\infty]_{p\text{-Me}}$ *vs.* $[\log k_0/k_\infty]_{p\text{-Cl}}$, *r* 0.998, slope 2.6) ensures a common mechanistic pattern. The free chlorine mechanism appears unlikely under the present conditions, since it could not discriminate between different sulphides given that k'_3 in eqn. (3) can hardly become rate limiting. On the contrary, these findings provide further support for step k_2 being the displacement of ArSMe by $>S'$ at the chlorine of $ArMeSCl^+$, since a lower selectivity is expected in the case of the better leaving group. This reaction mode appears even more likely from a comparison of the effects of sulphide structure on the rate with the effects of the same reaction performed in the absence of chloride ion (on the same substrates in aqueous dioxane under $HClO_4$ catalysis).[1b] Here a much more pronounced steric retarding effect (Et:Pr^n:Bu^n:Pr^i:3-pentyl, 0.7:0.8:1:0.013:0.00) is observed as a consequence of a different mode of reaction involving nucleophilic attack of sulphur on a sulphur atom. The rate-determining formation of intermediates such as $R^2R^3S^+–SArR^1Cl$ is therefore unlikely.

Experimental

Materials.—Reagent grade dialkyl sulphides and aryl methyl sulphides, obtained from the corresponding thiophenols according to literature procedures, were repeatedly distilled and their purity was checked by GLC. The aryl methyl sulphoxides, prepared by bromine oxidation of the corresponding sulphides in aqueous methanol[19a] or in two-phase water–methylene chloride in the presence of $KHCO_3$,[22] and (+)-(*R*)-methyl *p*-tolyl sulphoxide,[23] were repeatedly crystallized. Their physical constants corresponded to those reported in the literature. ^{18}O-Enriched methyl *p*-tolyl sulphoxide, prepared by $MeSO_3H$ catalysed oxidation of methyl *p*-tolyl sulphide with $H_2{}^{18}O_2$ in anhydrous ethanol,[24] was purified by thick layer chromatography on silica gel, with ethyl acetate as eluent and sublimed under reduced pressure.

Kinetic Measurements.—The progress of the reaction was monitored by recording the increase in optical density at the absorption maximum of the aryl methyl sulphide (253–258 nm) formed in the reaction. In the fast runs the reaction was followed for at least four half lives, and k_{obs} was calculated according to the Guggenheim method. Occasionally, the full range 220–270 nm was repeatedly recorded showing steady isosbestic points. The initial rate procedure was used in the slower experiments.

Protonation of Aryl Methyl Sulphoxides.—The protonation fractions were evaluated as described for aqueous solutions[7] and mixed solvents.[1a,b] ^{1}H NMR spectra (60 MHz) were recorded for solutions in $[^2H_4]MeOH–H_2O$ using $Me_3NH^+Cl^-$ as internal standard. The methyl group chemical shifts, measured in the presence of 0.5 mol dm^{-3} HCl and 14 mol dm^{-3} H_2SO_4 were assumed for the free base and the fully-ionized sulphoxide, respectively.

Reaction of ^{18}O- *and* (+)-(R)-p-*Tolyl Sulphoxides with* Me_2S. ^{18}O *and Optical Purity of the Unreacted Material.*—A 30 cm^3 solution of ^{18}O-labelled sulphoxide (6.0×10^{-3} mol dm^{-3}), Me_2S (3.6×10^{-2} mol dm^{-3}) and HCl (4 mol dm^{-3}) in $MeOH–H_2O$ (2:0.75, v/v) was allowed to react at 25 °C for 40 min, an half-life estimated from the relevant k_∞ value for the reduction reaction. After being quenched with aqueous sodium hydrogen carbonate, the sulphoxide was repeatedly extracted with $CHCl_3$ and isolated from the residue, after removal of solvent by medium-pressure chromatography, on a silica-gel column (using EtOAc as eluent) and was then sublimed. The ratio $(M + 2)/M\%$ was 20.6 ± 0.6 ($95 \pm 7\%$) as measured on a Micromass 16 VG mass spectrometer. The value was corrected for the natural isotopic abundance using the empirical relation $(M + 2)/M\% = 5.2 \pm 0.2$ for the unlabelled compound and also referred to the corrected value for starting material, in order to obtain the percentage label (reported in parentheses). The experiment was repeated: (*a*) in the absence of Me_2S to measure the extent of exchange with water, $(M + 2)/M\% = 14.3 \pm 0.5$ ($57 \pm 5\%$); and (*b*) in the absence of HCl but in the presence of Me_2S to check possible label loss during the sample handling and the isolation procedure: $(M + 2)/M\% = 21.1 \pm 0.6$ (assumed 100%).

Both experiments were also performed on the optically pure (+)-(*R*)-sulphoxide (7.6×10^{-3} mol dm^{-3}) which was allowed to react for 45 min in $MeOH–H_2O$ (2:0.75, v/v) and HCl (4.15 mol dm^{-3}) in the absence and in the presence of Me_2S (3.6×10^{-2} mol dm^{-3}). After chromatographic purification and sublimation, the polarimetric optical purities were measured.

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