Reduction and Racemisation of Sulphoxides by Halide Ions in Aqueous Perchloric Acid: First- and Second-order Dependence of Rates on h_0

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THE racemisation of optically active sulphoxides with HCl or HBr is considered to be due to a nucleophilic attack of halide ion on the protonated sulphoxide.[1] We have found that such a racemisation is related to the acid-catalysed reduction of sulphoxides by iodide ion, and that in both reactions the order on $[H^+]$ depends on the particular range of acid concentration and on the pK_a of the sulphoxide investigated,† while the rates are bound up with the relative thiophilicities (nucleophilicities towards sulphur) of the halide ions.

A detailed study of the reduction was carried out with *m*-chlorophenyl methyl sulphoxide (I) and *p*-tolyl methyl sulphoxide (II), in aqueous perchloric acid in a range of about 4 H_0 units. To avoid reversibility[2] an excess of I^- was employed, added as NaI. The order of reaction was found to be near to 1 in respect to $[I^-]$ at low and high acidities, when the salt effects on H_0 and rates were taken into account.‡ The reaction rates are strongly dependent on the acid concentration. They cannot be related to any simple function of the concentration, but in the extreme regions of acidity, log $k/[I^-]$ versus H_0 plots (k, first-order rate coefficients in sec.^{-1}) are linear with the following slopes (s): (I), $s = 1\cdot26$ at $H_0 = -4\cdot38$ to $-2\cdot78$ and $s = 2\cdot10$ at $H_0 = -1\cdot59$ to $-0\cdot51$; (II) $s = 1\cdot30$ at $H_0 = -3\cdot37$ to $-1\cdot85$ and $s = 2\cdot20$ at $H_0 = -1\cdot13$ to $0\cdot0$ [see Figure for the results with (II)].

Similar behaviour was found for the racemisation of (+) *p*-tolyl methyl sulphoxide (II)§ by chloride and bromide ions (added as sodium salts) in aqueous perchloric acid. The order of reaction on $[Cl^-]$ and $[Br^-]$ was found to be near to 1 in the whole range of acidity investigated, while at a fixed concentration of halide ions the slopes (s) were found again to be near to 1 at high acidity (Br^-, $s = 1\cdot31$ at $H_0 = -2$ to -3; Cl^-, $s = 0\cdot93$ at $H_0 = -3$ to $-4\cdot5$), and near to 2 at low acidity (Br^-, $s = 2\cdot16$ at $H_0 = -0\cdot5$ to $-1\cdot1$; Cl^-, $s = 2\cdot16$ at $H_0 = -0\cdot5$ to $-1\cdot3$).

Within the limits of validity of the Hammett acidity function H_0, the above slopes should mean that one and two protons are involved in the

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† Both first-order (D. Landini, G. Modena, F. Montanari, and G. Scorrano, *Tetrahedron Letters*, **1966**, 3309; S. Allenmark, *Acta Chem. Scand.*, 1961, **15**, 928) and second-order (J. H. Krueger, *Inorg. Chem.*, 1966, **5**, 137) dependence on $[H^+]$ has been reported for the reduction.

‡ The effect of iodide ion concentration on H_0 could not be directly measured because of its easy oxidisability, and data from measurements in the presence of NaCl were adopted (M. A. Paul and F. A. Long, *Chem. Rev.*, 1957, **57**, 1, 935).

§ Prepared with the Andersen's method (K. K. Andersen, W. Gaffield, N. E. Papanikolau, J. W. Foley, and R. I. Perkins, *J. Amer. Chem. Soc.*, 1964, **86**, 5637) $[\alpha_D]$ +145° (c1, acetone), m.p. 74—76°.

rate-determining step, equation (2), at high and low acidity, respectively.¶ Such findings may be explained by the following mechanism:

$$\rangle\mathrm{SO} + \mathrm{H}^+ \overset{\text{fast}}{\rightleftharpoons} \rangle\overset{+}{\mathrm{S}}\mathrm{OH} \qquad (1)$$

$$\rangle\overset{+}{\mathrm{S}}\mathrm{OH} + \mathrm{Hal}^- + \mathrm{H}^+ \xrightarrow{\text{slow}} \mathrm{Hal{-}}\overset{+}{\mathrm{S}}\langle + \mathrm{H_2O} \qquad (2)$$

$$\mathrm{Hal{-}}\overset{+}{\mathrm{S}}\langle + \mathrm{Hal}^- \xrightarrow{\text{fast}} \rangle\mathrm{S} + \mathrm{Hal_2} \qquad (3)$$

(reduction)

$$\mathrm{Hal{-}}\overset{+}{\mathrm{S}}\langle + \mathrm{Hal}^- \overset{\text{fast}}{\rightleftharpoons} \rangle\overset{+}{\mathrm{S}}\mathrm{{-}Hal} + \mathrm{Hal}^- \qquad (4)$$

(racemisation)

$$\rangle\overset{+}{\mathrm{S}}\mathrm{{-}Hal} + \mathrm{H_2O} \xrightarrow{\text{fast}} \mathrm{HO{-}}\overset{+}{\mathrm{S}}\langle + \mathrm{H}^+ + \mathrm{Hal}^- \qquad (5)$$

(racemisation)

The difference between reduction and racemisation is bound up with the fate of the halogenosulphonium ion: when Hal=I, a fast reduction to sulphide occurs with formation of molecular halogen, equation (3), but when Hal = Br or Cl, the reduction is much slower and the halogenosulphonium ion reverts to the starting material, equations (4) and (5). In the case of the bromide ion reaction, concurrent reduction was observed, but it was too slow to affect significantly the measured rates of racemisation. Fast halogen exchange equation (4), or, perhaps, the transient formation of di-halogenosulphides (R_2SHal_2) may account for the racemisation.

The suggested mechanism requires the general kinetic equation (6), which reduces to equation (7) at high acidity when the sulphoxide is fully protonated, and to equation (8) at low acidity, when the equilibrium constant of reaction (1) is to be taken into consideration:

$$\text{rate} = k[\rangle\overset{+}{\mathrm{S}}\mathrm{OH}]\,[\mathrm{Hal}^-]\,[\mathrm{H}^+] \qquad (6)$$

$$\text{rate} = k[\rangle\mathrm{SO}]\,[\mathrm{Hal}^-]\,[\mathrm{H}^+] \qquad (7)$$

$$\text{rate} = k/K_a\,[\rangle\mathrm{SO}]\,[\mathrm{Hal}^-]\,[\mathrm{H}^+]^2 \qquad (8)$$

Equation (7) and (8) correspond with satisfactory approximation to the equations experimentally found at high and low acidity, respectively, when $[\mathrm{H}^+]$ is substituted with h_0. It follows that, from the rate coefficients measured in the two ranges of acidity, the $\mathrm{p}K_a$'s of sulphoxides may be evaluated either graphically or numerically. In the case of the reduction by I^- they are: (I), $\mathrm{p}K_a = -2{\cdot}3 \pm 0{\cdot}15$; (II), $\mathrm{p}K_a = -1{\cdot}6 \pm 0{\cdot}15$. Values in the same range were found from the racemisations of (+)-(II) by bromide and chloride ions. They also are close to those recently reported by Andersen.[3] However, care should be taken in handling these results for the complexity of salt effects and the limits of validity of H_0 function in the case of sulphoxides.

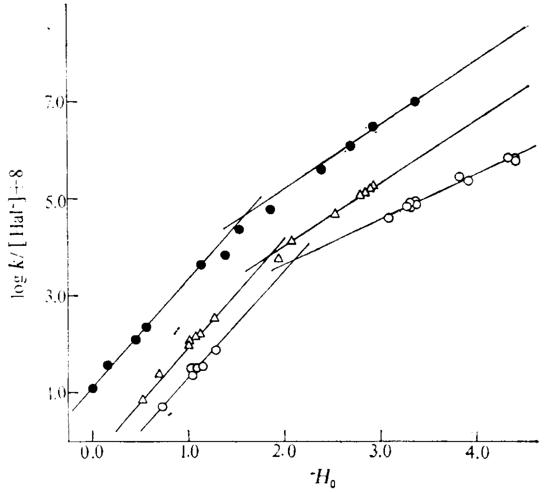

FIGURE. *Rates of reduction of* p-*tolyl methyl sulphoxide (II) by* I^- (●) *and of racemisation of* (+) p-*tolyl methyl sulphoxide by* Br^- (△) *and by* Cl^- (○) *in aqueous perchloric acid at* 25°.

Equation (2) represents a series of steps including the rate-determining one. Such a sequence may be considered either as a further protonation of $\rangle\overset{+}{\mathrm{S}}\mathrm{OH}$ followed by a rate-determining attack of Hal^-, equation (9),

$$\rangle\overset{+}{\mathrm{S}}\mathrm{OH} + \mathrm{H}^+ \rightleftarrows \rangle\overset{++}{\mathrm{S}}\mathrm{OH_2} \xrightarrow{\mathrm{Hal}^-} \mathrm{Hal{-}}\overset{+}{\mathrm{S}}\langle + \mathrm{H_2O} \qquad (9)$$

or as an attack of Hal^- followed by the expulsion of a molecule of water, subsequent to or concerted with a further protonation, equation (10).

$$\rangle\overset{+}{\mathrm{S}}\mathrm{OH} + \mathrm{Hal}^- \rightleftarrows \mathrm{Hal{-}}\overset{|}{\underset{|}{\mathrm{S}}}\mathrm{{-}OH} \xrightarrow{\mathrm{H}^+} \mathrm{Hal{-}}\overset{+}{\mathrm{S}}\langle + \mathrm{H_2O} \qquad (10)$$

It is not yet possible to make a choice between the two alternative mechanisms, because they

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¶ Such conclusions need, of course, further confirmation, particularly because the second protonation involves an acid–base equilibrium whose charge-type is different from that of the classical Hammett's bases. (See ‡).

require the same kinetics and very similar dependence on structural factors.** In particular, both of them are consistent with the large steric deceleration reported[2a,4] for the reduction with iodide ion, since both include a step in which Hal$^-$ attacks sulphur, probably from the rear.[2a]

The rates of racemisation as well as those of reduction of sulphoxides depend on the nucleophilic attack of halide ions on sulphur, and therefore the differences in rates should correspond to differences in nucleophilic power. The observed sequence $I^- > Br^- > Cl^-$, is the same as those reported for other reactions of halide ions in water at various electrophilic centres.[5]

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** Mechanism (9) is simpler and straightforward but, if the oxidation of sulphides by iodine (T. Higuchi and K. H. Gensch, *J. Amer. Chem. Soc.*, 1966, 88, 5486) is taken into consideration and the principle of microscopical reversibility applied, it demands that in the opposite reaction the attack of the water molecule on the halogenosulphonium ion displace the iodide ion forming the di-cation. This would mean that proton transfer is slower than removal of Hal$^-$. Mechanism (10) avoids this difficulty, allowing the proton transfer to be subsequent to or concerted with the attack of the water molecule.

[1] K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, jun., *J. Amer. Chem. Soc.*, 1964, **86**, 1452.

[2] (*a*) D. Landini, F. Montanari, H. Hogeveen, and G. Maccagnani, *Tetrahedron Letters*, 1964, 2691; (*b*) S. Allenmark, *Acta Chem. Scand.*, 1965, **19**, 1.

[3] K. K. Andersen, W. H. Edmonds, J. B. Biasotti, and R. A. Strecker, *J. Org. Chem.*, 1966, **31**, 2859.

[4] S. Allenmark, *Acta Chem. Scand.*, 1963, **17**, 2715.

[5] (*a*) J. D. Edwards and R. G. Pearson, *J. Amer. Chem. Soc.*, 1962, **84**, 16; (*b*) J. L. Kice and G. Guaraldi, *ibid.*, 1967, **89**, 4113.