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Steric Effects on the Reduction and on the Racemization of Sulphoxides

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THE reduction of sulphoxides by iodide ion has been shown¹ to be sensitive to steric factors at the sulphur atom. However, the complex dependence of reduction rates on the acid concentration and, further, the similarity of reduction by iodide ion to the racemization by bromide and chloride ions² caused us to re-examine the steric hindrance in these reactions under carefully controlled conditions. The sensitivity to steric hindrance and its magnitude is a key point in the understanding of the mechanism of the above reactions: high steric effects would support the hypothesis of rear-side attack at sulphur by halide ions (both in the reduction and in the racemization),^{1,2} whereas the suggested alternative³ of an attack at the oxygen atom would not require significant steric retardation, because of the crowding around the sulphur atom.

Alkyl phenyl sulphoxides, with increasing branching of the alkyl group (from Me to Bu^t), were chosen as substrates.

The rates of reduction of alkyl phenyl sulphoxides by iodide ion and the rates of racemization by chloride and bromide ions of the (+)-enantiomers were measured in aqueous perchloric acid (6M), in a medium of acidity such that the relatively small differences in basicity of the substrates are not likely to affect the rates significantly (Table).

of halide ions. The rates of this reaction for the methyl and isopropyl derivatives [k (sec.⁻¹) *ca.* 1×10^{-8} with 6M-HClO₄] were too low to affect the halide-ion catalysed reduction and racemization significantly.

It was also found that *t*-butyl phenyl sulphoxide loses optical activity at a much greater rate [k' (sec.⁻¹) *ca.* 80×10^{-8} with 6M-HClO₄] and the rate is hardly affected by the addition of halide ions. This means that the second-order coefficients for the halide ion-catalysed reduction and racemization of PhSOBu^t should be lower than 1.3×10^{-6} (sec.⁻¹ mole⁻¹ l.), a value which is obtained by dividing k' by the halide-ion concentration (0.6M). This limiting rate is more than one hundred times smaller than the observed reduction rate by I⁻ for PhSOPrⁱ under the same conditions.

Our results (Table) show that, in agreement with the previous work,¹ the reduction rate of sulphoxides by iodide ion is strongly depressed by α -ramification of the alkyl chain in the sulphoxide molecule. The relative rates are quite similar to those reported for other substitutions at the sulphur atom.^{4,5}

The rates of racemization are lower than those of reduction by a factor of about 30 for the reaction with bromide ions and of about 300 for the reaction with chloride ions.

Second-order rate coefficients ($k_{\text{Hal}} = k/[\text{Hal}]$, l.sec.⁻¹ mol.⁻¹) of reduction (k_I) and racemization (k_{Br} , k_{Cl}) of PhSOR catalyzed by acid halide ions, and first-order rate coefficient (k' , sec.⁻¹) of the acid-catalyzed reaction at 25°.

R =	Me	Pr ⁿ	Bu ⁱ	neo-C ₅ H ₁₁	Pr ⁱ	Bu ^t
$10^4 k_I$ ^a	340.0	258.0	153.0	14.0	5.8	—
$10^4 k_{\text{Br}}$ ^{b, d}	10.5	—	—	—	0.176	—
$10^4 k_{\text{Cl}}$ ^{c, d}	1.85	—	—	—	0.029	—
$10^4 k'$ ^d	0.0001	—	—	—	0.0001	0.008

^a [I] = 0.161M; [HClO₄] = 6.38M; ^b [Br⁻] = 0.6M; ^c [Cl⁻] = 0.6M; ^d [HClO₄] = 6.1M.

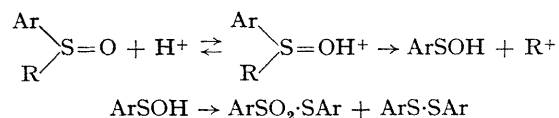
We observed that optically active sulphoxides lose optical activity in aqueous perchloric acid in the absence

The observed order is the one expected for the nucleophilicity of the halide ions.⁶ The decrease in reactivity is

quite similar in the three reactions investigated in passing from methyl to isopropyl derivatives. This would indicate that the reduction and the racemization have similar transition states and that in both reactions rear-side attack of the halide ion on the sulphur atom is involved.

As indicated above it was not possible to extend the comparison to *t*-butyl derivative. It was proved that in the conditions followed, it decomposes to diphenyl disulphide and *S*-phenyl benzenethiosulphonate. The reaction rate depends on acid concentration ($k' = 0.8$ and 4.1×10^{-6} with 6.1 and 8.6M-HClO₄ respectively). When the reaction was stopped at about 80% completion, the undecomposed *t*-butyl sulphoxide was shown to have a specific rotation at least 90% that of the starting material.

These results are consistent with the following scheme:†



The hypothesis is supported by the large effect of the alkyl group on the rate of decomposition (related to the stability of the corresponding cation) and is connected with the fairly easy heterolysis of the sulphur-carbon bond in some related reactions.⁷

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† The alternative hypothesis (E. G. Miller, D. R. Rayner, H. T. Thomas, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4861; D. J. Abbott and C. J. Stirling, *Chem. Comm.*, 1968, 165) of a mechanism based on the homolysis of the SO-R bond, formally similar to that above, is not consistent with our data. Also Oae's suggestion (S. Oae and N. Kunieda, *Bull. Chem. Soc. Japan*, 1968, **41**, 696; S. Oae, M. Yokoyama, and M. Kise, *ibid.*, p. 1221) of racemization of sulphoxides *via* the ion SOH₂²⁺ is not satisfactory in the present case.

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