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KINETICS AND MECHANISM OF THE REDUCTION OF SULPHOXIDES BY HYDRIODIC ACID

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A kinetic investigation of the reduction of sulphoxides to sulphides by hydriodic acid in aqueous acetic acid solution is reported.

The reaction ($>SO + 2HI \rightarrow >S + I_2 + H_2O$) follows a third-order rate process (first-order with respect to sulphoxides (1), second-order with respect to hydriodic acid), and is acid-catalysed. The reaction rate is depressed by addition of water, and is considerably affected by steric factors. The reactions were carried out under hydrogen atmosphere and followed by titration of the iodine with sodium thiosulphate, as previously described (2).

The pseudo-first-order rate constants of the reduction of meta- and para-substituted phenyl-methyl-sulphoxides are reported in Table 1. The values fit well the Hammett equation ($\rho = -0.931$). The third-order rate constants of phenyl-methyl- and dimethyl-sulphoxide, and the effect of

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TABLE 1

Pseudo-first-order rate constants in 77.4% (v/v) acetic acid-water at 25.0°

$c_{SO} = 7 \times 10^{-3}$ M/l.; $c_{HI} = 3.89 \times 10^{-1}$ M/l.

R	$k_1 \times 10^4$ sec.$^{-1}$	R	$k_1 \times 10^4$ sec.$^{-1}$
p-OH	1.87	m-OH	0.95
p-OCH_3	1.95	m-OCH_3	0.87
p-CH_3	1.80	p-Cl	0.60
p-$C(CH_3)_3$	1.48	m-Cl	0.42
m-CH_3	1.35	m-NO_2	0.20
H	1.33	p-NO_2	0.30

TABLE 2

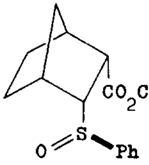
Third-order rate constants in 95% (v/v) acetic acid-water at 25.0°

$c_{SO} = 1.19 \times 10^{-2}$ M/l.; $c_{HI} = 2.28 \times 10^{-2}$ M/l.

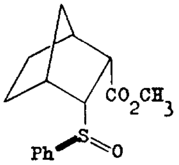
Sulphoxide	$c_{F_3C-CO_2H}$(M/l.)	$k_3[(M/l.)^{-2}sec.^{-1}]$
C_6H_5-SO-CH_3	-	0.68
CH_3-SO-CH_3	-	1.86
CH_3-SO-CH_3	6.3×10^{-2}	2.49
CH_3-SO-CH_3	25.0×10^{-2}	3.58

trifluoroacetic acid on the reduction rate of dimethyl-sulphoxide are reported in Table 2. With an excess of sulphoxide the reduction follows a second-order equation with respect to hydriodic acid: $k_2^{25°}$'s for Me-SO-Me and Ph-SO-Me are 2.78×10^{-2} and 1.58×10^{-2} $(M/l.)^{-1}$ sec.$^{-1}$, respectively (c_{SO} =

5.86×10^{-1} M/l., $c_{HI} = 2.32 \times 10^{-2}$ M/l.). The influence of the water content of the medium is indicated by the following values of $k_1^{25°}$, in sec.$^{-1}$: 2.43×10^{-3} (17.6%); 0.36×10^{-3} (22.6%); 0.058×10^{-3} (26.6%). The influence of steric effects is indicated by the relative rates of reduction of phenyl--alkyl-sulphoxides, measured in the conditions reported in Table 1: Alk = Me (100), Et (81), i-Pr (1.8), t-But (0.07).



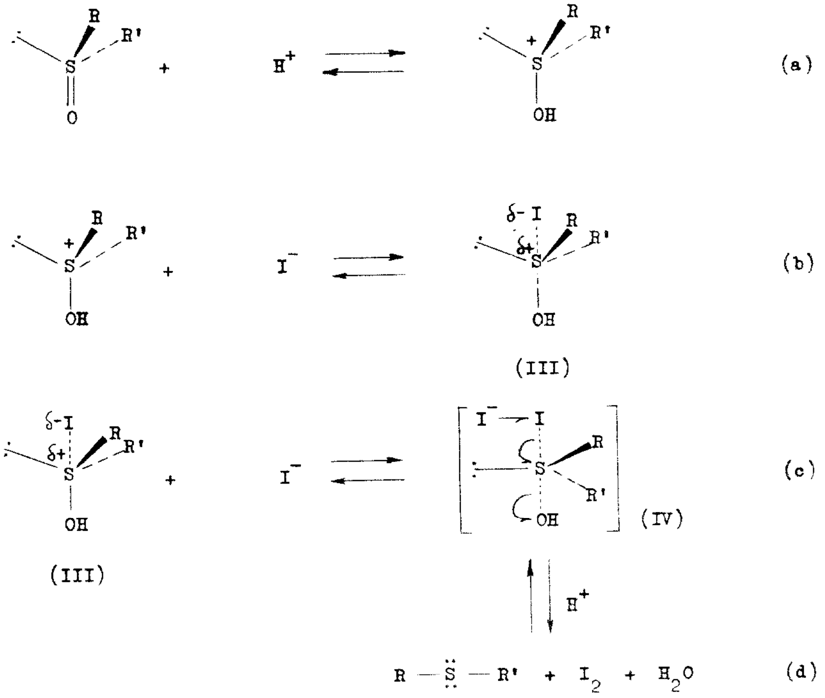
syn (I)



anti (II)

The reduction of bicyclic sulphoxides (I) and (II), with known configuration at the sulphur atom (3,4), gave indications on the stereochemistry of the reaction. In the same conditions reported above, the values of $k_1^{25°}$'s are 18.4×10^{-5} sec.$^{-1}$ for the *syn*-isomer (I), and 4.0×10^{-5} sec.$^{-1}$ for the *anti*-isomer (II), respectively. An opposite reactivity was found with bis--(1,2-dimethylpropyl)borane: the *anti*-isomer is reduced to the corresponding sulphide, while the *syn*-isomer is unaffected (3). The borane must attack the center of highest electron density, which is the sulphinyl-oxygen (3,5). Since the oxygen is less sterically hindered in the *anti*- than in the *syn*--isomer, the inversion of the reactivity of the two isomers, going from borane to hydriodic acid, seems to indicate that in the latter case the steric effects are localised in the opposite region with respect to the sulphinyl-oxygen.

On the basis of the kinetic and stereochemical data the following reaction mechanism is proposed:



The slowest step (c) should consist of an electron transfer from the iodine to the sulphur atom promoted by a second iodine ion, and elimination of the OH group, according to a mechanism which would be formally similar to a S_N2 substitution at the carbon atom; the negative sign of ρ indicates that the positive charge on the sulphur atom is larger in the transition than in the initial state. In other words the S-OH bond cleavage tends to precede the electron transfer from iodine to sulphur. On the basis of the proposed model for tetracoordinated sulphur (6), the transition state (IV) is likely to possess a bipyramidal structure, with I and OH lying on a straight-line passing through the sulphur atom.

The formation of sulphoxide complexes coordinated through the oxygen atom (5), and of charge transfer complexes between sulphoxides and iodine, iodine cianide, and iodine monochloride, respectively (7), agrees with the existence of the equilibria (a) and (b). It should be noted that the representation of the intermediate (III) is somewhat arbitrary, and that the tendency of (III) to approach a bipyramidal structure probably depend on the amount of covalent character of the S....I bond.

If the molar concentration of hydriodic acid does not exceed the concentration of sulphoxide, the reaction is reversed when the medium is diluted with water, and the kinetics of reduction can be correctly followed only if the samples are poured in water containing iodine ions (no appreciable reduction takes place in these conditions).

Our data and those recently reported by Mislow (8) allow a complete understanding of the behaviour of sulphoxides with halo-acids, the overall picture being as follows: no reaction with HF, fast racemisation with HCl, racemisation and reduction with HBr, complete reduction with HI. This agrees with the different reducing power of the halide ions (greatest for I^-, lowest for F^-), and with the assumed stability of the S-halg bonds, which is expected to be maximum for S-Cl. It should be noted that, in the reaction of optically active p-tolyl-benzyl-sulphoxide (α_D = + 245°) (9) with HI, loss of optical activity strictly parallels reduction: this means that a stable intermediate $(RR'SI)^{+}I^{-}$ or $RR'SI_2$, similar to those proposed by Mislow (8) for the racemisation of sulphoxides by HCl, cannot be formed.

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