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OXIDATION OF ORGANIC SULPHIDES - XI[1]

OXIDATION OF SULPHOXIDES IN ALKALINE SOLUTION

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In previous research[2] it was shown that the mechanism of the oxidation of sulphoxides to sulphones in neutral or acidic solutions involves a nucleophilic attack of the sulphur atom on the peroxyacid; the same conclusions were reached by G. Kresze, W. Schramm and G. Cleve[3]. Research now in progress shows that in alkaline solutions the oxidation may occur with a second mechanism characterized by a nucleophilic attack of the anion of the peroxyacid on the SO group[4].

J. F. Goodman and co-workers[5] showed that the peroxybenzoic acid decomposition in alkaline solutions is in fact a reaction of the anion with the undissociated peracid molecule and that the velocity reaches a maximum when equal amounts of the two species are present, i.e. at a pH equal to the pK_a.

The velocity of the oxidation of p-nitrodiphenyl-sulphoxide with peroxybenzoic acid in dioxane-water (40:60) in alkaline solutions follows an overall second order kinetics and the reaction rate increases steadily with the apparent pH of the solution[6] up to about pH 10, then a further increase in pH has practically no effect on the rate (see Fig. 1). The reaction coefficient is, of course, complex but to a first approximation this may be ignored.

The peroxybenzoic acid alone in dioxane-water (40:60) decomposes so slowly that it does not interfere in the measured rate of oxidation of sulphoxides. However the rate of decomposition varies with the pH (on the alkaline side) in the same way as shown by Goodman and co-workers[5]. Of course the pH for the maximum rate in the mixed solvent is not the same as the pH for the maximum rate in water (see Fig. 2).

It seems safe to assume that in dioxane-water as in water the pH at which the autodecomposition of peroxybenzoic acid reaches a maximum corresponds to the pK_a of the peroxyacid.

Comparing Figs 1 and 2 it is easy to see that the maximum rate of sulphoxide

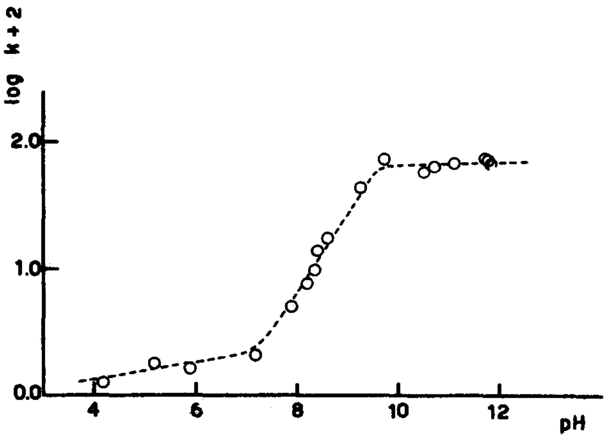

Fig.1

Rates of oxidation of p-nitrodiphenylsulphoxide with peroxybenzoic acid in dioxane-water (40:60) at 25.0° at various pH's.

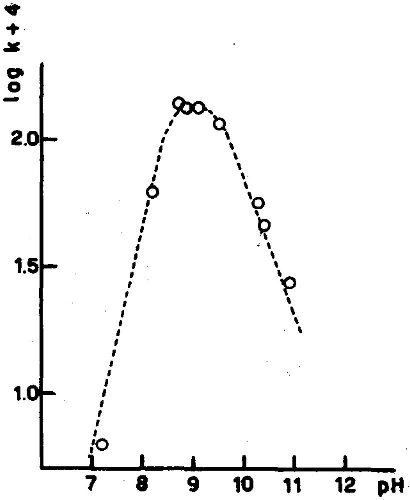

Fig.2

Variation with pH of decomposition rate of peroxybenzoic acid in dioxane-water (40:60) at 25.0°.

oxidation is reached at 1 - 2 pH units higher than that for the maximum decomposition of peroxybenzoic acid, i.e. when the peroxyacid is almost completely transformed into its anion.

As expected the effect of substituents in the rate of oxidation of diphenylsulphoxides in alkaline solution is the opposite of that found in neutral solutions[2] and is such that electronwithdrawing groups increase the reaction rate (see Table). The substituent effect follows the Hammett relation with $\rho = -0.69$.

TABLE

Rate of oxidation of substituted diphenylsulphoxides with peroxybenzoic acid in dioxane-water (40:60) at pH = 11.72 ± 0.05

Substituent	p-OCH_3	p-CH_3	H	p-Cl	m-Cl	m-NO_2	p-NO_2
$k_2 \times 10$ (1 mole^{-1}sec^{-1})	1.46	1.49	1.60	2.99	3.12	6.70	7.22

These results clearly show that the anion of peroxybenzoic acid is a stronger oxidizing agent for sulphoxides than the neutral molecule, while the opposite is the case in the oxidation of sulphides, where the rate decreases strongly with increasing pH[7].

It seems therefore that the SO group may be oxidized by an electrophilic attack by peroxybenzoic acid in neutral solution with a mechanism analogous to the oxidation of sulphides[8] and tertiary amines[9] and that it may be also oxidized by a nucleophilic attack of the peroxyacid anion with a mechanism which resembles the oxidation of ketones[10].

Researches are in progress to elucidate the many aspects of this new reaction and the results will be reported shortly.

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