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OXIDATION OF ORGANIC SULPHIDES - XII[*] :
OXIDATION OF PHENYL METHYL SULPHOXIDES IN AQUEOUS ALKALINE SOLUTION BY PEROXYBENZOIC ACID

R. Curci and G. Modena
Istituto di Chimica Organica
Universitá di Bari

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In recent papers the first example of oxidation of sulphoxides in alkaline medium with peroxybenzoic acid has been reported[1].

The reaction was studied in dioxane-water as solvent in the (apparent) pH range 4-12 . Contrary to sulphides, amine, etc., sulphoxides, or at least those considered[2], reacted faster in alkaline than in neutral or acidic medium. The pH in the ranges 4-7 and 10-12 did not significantly affect the rates while the velocity was strongly increased in the range 7-10.

At pH above 10 the effect of substituents in diphenylsulphoxides is characterized by a positive value of "rho" (+ 0.71) while in neutral solution a negative value of "rho" (- 0.54) has been found[3].

Althought a rigorous treatement of the data was not attempted , it was clearly shown that the oxidation of sulphoxides follows equation I in the pH range :

$$\text{I)}\quad v = k_{ac}\left[R_2SO\right]\left[RCO_3H\right] + k_{alk}\left[R_2SO\right]\left[RCO_3^-\right]$$

On the basis of these evidences it was suggested that the sulphoxides are oxidized electrophilically by undissociated peroxyacid and nucleophilically by the anion of it.

The proposed mechanism is confirmed by the present study on the oxidation in (pure) water of phenyl methyl sulphoxides with peroxybenzoic acid in the pH range 4-11 . The results are shown in tables 1, 2, and 3 and fig. 1 .

Phosphate and borate buffers as well as sodium hydroxide were employed ; in the range of concetration used the buffers have practically no effect on the rates (see table 2) nor the autodecomposition of peroxybenzoic acid contributes significantly to the disappearence of the peracid. Therefore no correction was necessary and the rate coefficients were calculated as previously described[1].

The effect of pH on the rates of oxidation follows the same trend earlier observed for the reactions in dioxane-water[1], however in the present case, as the pK_a value of peroxybenzoic acid was measured with good accuracy[4] and there are not uncertainties in the meaning of pH , behaviour of electrolites, etc., it was possible to calculate from equation 1 the theoretical curve, which matches, as shown in fig. 1 , the experimental points very well.

TABLE 1

Oxidation Rates of Phenyl Methyl Sulphoxide in Water at 25.0°

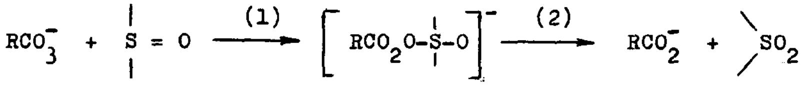
Buffer	pH	k x 10
Ftalate/NaOH	4.20	0.33
"	5.00	0.34
"	6.10	0.46
KH_2PO_4/NaOH	7.25	1.32 (a)
"	7.70	3.01 (a)
"	7.80	3.85 (a)
H_3BO_3/NaOH	8.85	4.19 (a)
"	9.95	5.05 (a)
"	10.00	5.15 (a)
NaOH	10.80	5.41 (a)
"	11.95	5.30 (a)

Reagent concentrations ~ 3×10^{-3}M ; k in $mole^{-1}sec^{-1}l$;
(a) EDTA added ~ 1×10^{-4}M .

The effect of substituent in the phenyl methyl sulphoxides at pH 10 follows the Hammett relationship with "rho" = + 0.38 .

Our results for the alkaline oxidation are consistent with the general schema II , already proposed[1] :

II)



$$RCO_3^- + \overset{|}{\underset{|}{S}}=O \xrightarrow{(1)} \left[RCO_2O-\overset{|}{\underset{|}{S}}-O\right]^- \xrightarrow{(2)} RCO_2^- + >SO_2$$

TABLE 2

Effect of Buffers on the Oxidation Rates of Phenyl Methyl Sulphoxide [SO] with Peroxybenzoic Acid [PBA] in Water at 25.0° .

[SO] (mole/l)x10^3	[PBA] (mole/l)x10^3	[H_3BO_3] (mole/l)	[NaOH] (mole/l)	pH	k (mole^{-1}sec^{-1}l
3.16	2.62	0.055	0.048	9.98	0.505
3.35	3.08	0.110	0.098	10.02	0.514
3.31	2.62	0.220	0.197	10.15	0.470

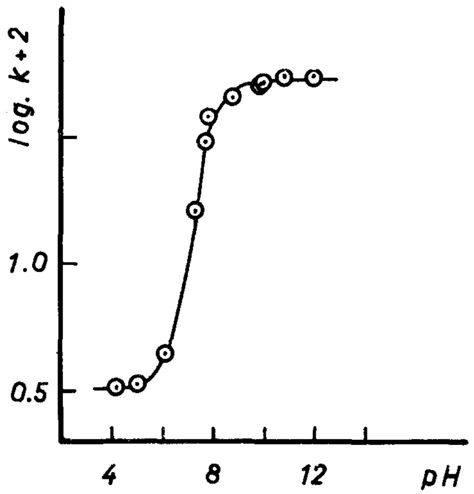


FIG. 1

Oxidation Rates of Phenyl Methyl Sulphoxide with Peroxybenzoic Acid in Water at 25.0° at Various pH's .

TABLE 3

Effect of Substituent on the Oxidation Rates of $X-C_6H_4-SO-CH_3$ at pH 10 in Water at 25.0°

X =	p-CH_3	H	p-Cl	p-Br	m-NO_2
k x 10 (mole^{-1}sec^{-1}l)	4.88	5.14	6.54	6.40	10.2

"rho" = +0.38 ; r = 0.99 ; s = 0.02

The nucleophilic attack on the sulphoxide group is supported by the high and constant rate at high pH where the anion of the peracid is the only species present and by the effect of the substituent on the sulphoxide group. We have, at the moment, only preliminary results on the substituent effect in the peroxybenzoic nucleus from which a provisional "rho" value of about +0.4 may be evaluated.

It, of course, should mean that the heterolysis of the O-O bond is within the rate determining step or perhaps that it is the slow step: in this case reaction 1 would be a preequilibrium.

Similar results have been recently reported by P. Robson[5] for the alkaline oxidation of sodium o-sulpho-benzaldeyde and he suggested a quite similar mechanism .

A more detailed analysis of our findings, together with the results of research on the steric requirements of the alkaline oxidation of sulphoxides, now in progress in this laboratory, will be published elsewhere .

REFERENCES

* Work sponsored by C.N.R.

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