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OXYGEN EXCHANGE AND RACEMISATION OF 4-METHOXYDIPHENYLMETHANOL IN MOIST ACIDIC DIOXAN

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THE rates of oxygen exchange and racemisation of 4-methoxydiphenylmethanol are the same in acidic aqueous dioxan of high water content.[1] But the racemisation of 4-chlorodiphenylmethyl chloride is generally faster than substitution in solvents of low water content, presumably because racemisation may occur in an ion-pair which may collapse with internal return to a racemic reactant.[2] The displaced group in the acid catalysed heterolysis of an alcohol initially carries a formal positive charge, and therefore the fragments in the hypothetical intermediate (I) cannot be held together by the attraction of unlike charges:

$$\mathrm{ROH} + \overset{+}{\mathrm{H}} \rightleftharpoons \overset{+}{\mathrm{ROH}_2} \rightleftharpoons \underset{\mathrm{I}}{\left[\mathrm{R} - - - \mathrm{OH}_2\right]^{+}} \rightleftharpoons \overset{+}{\mathrm{R}} + \mathrm{H}_2\mathrm{O}$$

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[1] C.A. Bunton, D.R. Llewellyn and I. Wilson, *J.Chem.Soc.*, 4747 (1958).

[2] S. Winstein, J.S. Gall, S.Smith and M. Hojo, *J.Amer.Chem.Soc.*, **82**, 1010 (1960); S. Winstein, M. Hojo and S. Smith, *Tetrahedron Letters*, No.22, 12 (1960).

The rate constants of racemisation, k_R, and of oxygen exchange, k_E, are in the Table, and in solvents of low water content and acidity

TABLE

Rate constants of exchange and racemisation at 25.0° unless specified.

Expt. No.	1 - 4	5-6,9-10	11 - 13[*]	14- 16	
% Dioxan v/v	98.01	95.80	95.80	90.0	60.0
$[HClO_4]$ M	0.050	0.105	0.200	0.101	0.101
$10^4 k_R$ sec.$^{-1}$	31,30	14,13	14,15	1.5,1.3	0.82[+]
$10^4 k_E$ sec.$^{-1}$	24,23	7.5, 7.0	17	1.5	0.80[+]

[*] 15.0°. [+] ref. 1

$k_R/k_E > 1$. We exclude an S_N2 reaction which should give complete inversion of configuration,[‡] both on structural grounds, and because k_R/k_E depends on the solvent composition (Ref. 1 and Table), and therefore conclude that internal return is taking place.[*]

The stereochemistry of the exchange will depend upon the life-time of the carbonium ion intermediate (I), and the time required for the expelled water molecule to migrate from the solvation shell of the carbonium ion and so lose its identity in the solvent. In aqueous

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[‡] C.K. Ingold, Structure and Mechanism in Organic Chemistry, Bell, London, 1953, p.377.

solvent the ion is captured by a water molecule attacking impartially from front or rear,[3] but in the drier solvents, where $k_R/k_E > 1$, recapture must occur to some extent by the original water molecule attacking impartially from either direction. (Recapture by the original water molecule from the front will have neither stereochemical nor isotopic consequences, and specific capture by a solvent molecule from the rear is improbable because of the behaviour in more aqueous solvents).

The effects on k_R/k_E can now be understood, because as the water content is decreased the expelled water molecule will be slower to equilibriate with the relatively few water molecules of the solvent, and the carbonium ion will lose its stereochemical identity, but rejoin its original partner. (Expts. 1-10). But when the water content is further decreased, or the water activity decreased by added acid, the carbonium ion will be solvated predominantly by dioxan molecules. Then the expelled water molecule will again equilibriate with the solvent, and recapture of the carbonium ion will be stereochemically non-specific, and $k_R/k_E > 1$. (Expts. 11-13).

There is considerable kinetic evidence that "encumbered", rather than free carbonium ions are intermediates in many acid catalysed reactions of alcohols,[4] and the intermediates which we discuss may be

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[4] R.H. Boyd, R.W. Taft, A.P. Wolf and D.R. Christman, *J.Amer.Chem.Soc.*, **82**, 4279 (1960), and ref. cited.

regarded in this light. There is stereochemical and spectroscopic evidence for the solvation of carbonium ions by ethers.[5]

The rates of exchange and racemisation increase sharply with decreasing water content of the solvent (Table and ref.1). This behaviour is typical of acid catalysed reactions, and the protonating power of the medium, as measured by $-H_0$, increases similarly.[6]

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[5] A. Streitwieser and S. Andreades, J. Amer.Chem.Soc., 80, 6553 (1958) ; W.B. Smith and P.S. Rao, J.Org.Chem., 26, 254 (1961).

[6] Long and Paul, Chem. Rev., 57, 935 (1957).