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BIMOLECULAR KINETICS DURING THE ACID-CATALYZED DEHYDRATION OF ALCOHOLS

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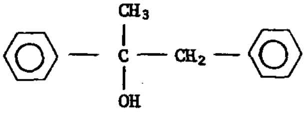
The acid-catalyzed dehydration of 1,2-diphenyl-2-propanol, 1, when performed under kinetically controlled conditions, produces a 1:1 mixture of trans-α-methyl-stilbene and α-benzylstyrene (1). During our study of this dehydration, we became interested in the effect of substituents in the aromatic rings upon the rate of dehydration. In preparation for this study, the kinetics of the dehydration of 1 was examined in some detail.



1

Dehydration of the alcohol was effected in acetonitrile using p-toluenesulfonic acid as a catalyst. The reaction progressed at a convenient rate in the temperature range of 50-70° and samples, withdrawn periodically, were quenched on anhydrous sodium carbonate and analyzed by v.p.c. (2).

Analysis of the data showed that the alcohol reacted at a rate which was neither uniformly first order nor uniformly second order in the alcohol. Instead, the first portion (ca. 60%) of the reaction showed a second-order dependence on the alcohol concentration, the last portion (ca. 30%), a first-order dependence with, of course, a transitional region separating the two portions.

As an explanation of this kinetic behaviour, the following sequence of reactions appears to be the simplest:

$$ROH + H^{+} \rightleftarrows R\overset{+}{O}H_2 \rightleftarrows R^{+} + H_2O; \quad K_1 \qquad .....1$$

$$R^{+} + ROH \rightleftarrows R_2\overset{+}{O}H; \quad K_2 \qquad .....2$$

$$R^{+} \rightarrow H^{+} + \text{product}; \quad k_1 \qquad .....3$$

$$R_2\overset{+}{O}H \rightarrow R\overset{+}{O}H_2 + \text{product}: \quad k_2 \qquad .....4$$

Two equilibria are suggested, one involving reversible carbonium ion formation, the other reversible ether (protonated) formation through the carbonium ion. Two rate controlling steps follow, one the rate-controlling loss of a proton from the carbonium ion as suggested by Noyce (3) for a similar alcohol, the other a rate-controlling decomposition of the protonated ether to alkenes.

The overall kinetic expression contains two terms, a first-order term due to equations 1 and 3 and a second-order term due to equations 1, 2 and 4. As the reaction progresses and the

$$\frac{-d[\mathrm{ROH}]}{dt} = \frac{k_1K_1}{[\mathrm{H_2O}]}[\mathrm{H^+}][\mathrm{ROH}] + \frac{k_2K_1K_2}{[\mathrm{H_2O}]}[\mathrm{H^+}][\mathrm{ROH}]^2$$

$$= k_1'[\mathrm{H^+}][\mathrm{ROH}] + k_2'[\mathrm{H^+}][\mathrm{ROH}]^2$$

alcohol concentration decreases, the partial rate due to the bimolecular portion surrenders its dominant role to the unimolecular portion. The concentration of water is an important feature of the pseudo-first and pseudo-second-order rate constants. Contributions to this are made by the catalyst, the solvent and by the dehydration itself

i.e. $[\mathrm{H_2O}] = [\mathrm{H_2O}]_{\text{solvent}} + [\mathrm{H_2O}]_{\text{catalyst}} + [\mathrm{H_2O}]_{\text{reaction}} = [\mathrm{H_2O}]_0 + [\mathrm{H_2O}]_{\text{reaction}}$

At any particular time t, the concentration of water

$$[\mathrm{H_2O}]_t = [\mathrm{H_2O}]_0 + [\mathrm{ROH}]_0 - [\mathrm{ROH}]_t$$

and to a first approximation remains constant throughout the reaction and equal to the sum $[\mathrm{H_2O}]_0 + [\mathrm{ROH}]_0$.

Pseudo-Rate Constants for the Dehydration at 50°C.

$[\mathrm{ROH}]_0^a$	k_2'	k_1'
0.668	0.0186	0.00475
0.334	0.101	0.0116
0.186	0.354	0.0273
0.067	1.616	0.0538
0.334^b	-	0.00407
0.334^c	No reaction	No reaction

a) all runs 0.0186 M in p-toluenesulfonic acid

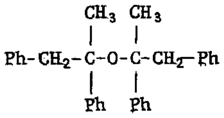
b) 0.334 M in water.

c) 5.25 M in water.

An examination of the data of the Table shows the dependence of the pseudo-rate constants upon the initial alcohol concentration; as the initial concentration decreases, the rate constants increase. Again, adding water initially to the system should decrease both pseudo rate constants. In one experiment performed, a large concentration of water inhibited the dehydration completely. If the amount of water added is equimolar with the alcohol, the kinetics become chiefly first-order in alcohol concentration since the carbonium ion is largely confined to the equilibrium of equation 1 unless it escapes by decomposition as in equation 3. This undoubtedly explains why Noyce (3) observed only first-order dependence in the acid-catalyzed decomposition of 1,2-diphenylethanol since he employed aqueous ethanol as solvent.

Broadly speaking, ethers are considered relatively stable compounds particularly under the mild conditions employed in these experiments. More direct evidence that an ether may form and decompose under the conditions of dehydration was obtained by carrying out the reaction in benzene-methanol. The methyl ether, 2-methoxy-1,2-diphenylpropane, was formed in amounts as high as 25% of the reaction products before it too decomposed to the alkene mixture. This methyl ether was isolated and its rate of decomposition, measured under conditions identical to those used for the dehydration of 1, proved to be approximately half that of the alcohol itself.

The postulated intermediate, the protonated bis-tertiary ether 2, would be expected to be much less stable than the methyl ether. However, if its rate of decomposition were not greatly in excess of that of the alcohol, a measurable concentration should be formed at some point during the dehydration and treatment with base would convert it to the ether 2.



$$\mathrm{Ph{-}CH_2{-}\underset{Ph}{\overset{CH_3}{C}}{-}O{-}\underset{Ph}{\overset{CH_3}{C}}{-}CH_2{-}Ph}$$

2

Using t.l.c. (4), the reaction mixture was examined during the course of the dehydration. A small amount of a product which was neither the original alcohol nor the product alkenes was indeed formed during the reaction but disappeared before dehydration of the alcohol was complete. This material was isolated from a large experiment by a combination of crystallization and column chromatography (∿.05% yield) and its spectral properties and analytical data were compatible with the structure 2.

Thus the demonstrated presence of the bis-tertiary ether 2, the sensitivity of the methyl ether to acids, and the observed bimolecular kinetics, all indicate that the dehydration of the alcohol 1 can proceed, at least in part, through the intermediate $R_2\overset{+}{O}H$, the protonated form of ether 2.

While ether formation during acid-catalyzed dehydrations is not an unknown occurrence(6), it is believed that this is the first indication that a protonated ether can be considered as an intermediate in the dehydration of an alcohol. In this instance, its appearance is no doubt a rather special case and is related both to the relative longevity of the carbonium ion and to the fact that the ether, being a bis-tertiary benzylic ether, readily decomposes.

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1. I. Ho and J.G. Smith, Tetrahedron (in press).
2. Analyses were performed on a Varian-Aerograph 1520 gas chromatograph with flame-ionization detectors using a 5 ft. by 1/8 inch column packed with 10% Carbowax 20M on Chrom W with a column temperature of 165°. Peak areas were measured by a Disc integrator and corrected by a detector response factor determined with standard samples.
3. D.S. Noyce, D.R. Hartter and R.M. Pollack, J. Am. Chem. Soc., 90, 3791, 3794 (1968).
4. Thin-Layer chromatography was carried out using Eastman Chromagram Sheet 6060 (silica gel with fluorescent indicator) with hexane containing 5% benzene as developing solvent.
5. Anal. Calcd. for $C_{30}H_{30}O$: C, 88.61; H, 7.44.
   Found: C, 88.70; H, 7.64.
   The i.r. spectrum showed a C-O stretching band at 1070 cm^{-1}, strong aliphatic C-H absorption bands in the 3000-2850 cm^{-1} region but no absorption due to an -OH group. In overall appearance the spectrum resembled that of the methyl ether.
6. For example, W. Wuyts, Bull. Soc. Chim. Belg., 30, 176 (1921).
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