β-Deuterium Isotope Effect in Solvolysis of α-Phenylethyl Chloride: the Nature of the Transition State in Solvolysis

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THE nature of the transition state in solvolyses has been the subject of a long controversy between American and English workers. To date, as far as we are aware, the matter has not yet been settled unambiguously, although a recent publication by Okamoto[1] and his co-workers seems to favour the dual mechanism supported by the English school.

Recently, Professor Whiting, in his Tilden Lecture,[2] has summarized both points of views drawing attention to what he calls a "real, interesting and important difference in emphasis in the views expressed on this most fundamental reaction".

During preliminary research on secondary deuterium isotope effect on racemisation rates of α-phenylethyl chloride, we have measured the solvolysis rate of α-phenylethyl chloride and [2,2,2-$^2H_3$]-α-phenylethyl chloride in ethanol–water mixtures containing from 0 to 10% water (in volume per cent).

The isotope effect in this reaction has already been measured by Shiner and Murr[3] for solvent composition ranging from 50 to 80% ethanol. The ratio of rates k_H/k_D has been found remarkably constant around 1·22.

On the basis of what is known about isotope effects and solvolysis reactions, we were expecting a slow and monotonic decrease of this ratio. Although the value, and even the sign, of the secondary isotope effect is not yet quite certain for S_N2 reactions, it seems established beyond any reasonable doubt that hyperconjugative stabilization of the carbonium ion is the main cause of this effect during S_N1 solvolysis. Anyway, if, as we believed at the outset, the α-phenylethyl chloride is a "border line" case, there will be a smooth transition between a limiting S_N1 solvolysis in 80% ethanol to an almost limiting S_N2 solvolysis in pure ethanol. In any case, we were anticipating an isotope effect *monotonically* decreasing from 1·22 to something around 1·00 (0·90 to 1·10).

Our findings, at 50° (see Table), have been quite different.

We find it impossible to fit our results within the scheme of the push–pull mechanism suggested by the American workers. Instead we think that the sharp increase in the isotope effect in water-poor mixtures shows that:

(i) The solvolysis reaction is a competition between two different reactions, a unimolecular one and a bimolecular one,

(ii) The bimolecular reaction has a rather high activation energy and plays a significant role only at the last moment, when the "ionizing" power of the solvent is unable to promote the breaking of the C–Cl bond, that is in mixtures containing less than 5% water.

(iii) The transition state nears that of the carbonium ion when the water content of the solvent decreases from 20 to 5%. This is not surprising since as the dielectric constant of the solvent and its "ionizing power" (measured for example by the Grunwald-Winstein's Y parameter) decreases, a more important separation of charges is needed to obtain the same "solvation energy".

One question remains unanswered: the nature of the bimolecular reaction; we can imagine two different reaction paths: a triangular bipyramidal transition state, as in a classical S_N2 reaction, or a transition state resulting from a nucleophilic attack on a tight ion-pair.

If this interpretation is correct, we can foresee the following:

(*a*) The same increase for the α-deuterium isotope effect as will be observed the "ionizing power" of the solvent is lowered. The fact that this α-effect is only 1·15 in 80% ethanol[3] instead of around 1·38 for a "true" carbonium ion as calculated by Streitwieser,[4] shows that the transition

TABLE

% H_2O (in volume)	10	8	6	5	4	2	0
f H_2O (mole fraction of H_2O) ..	0·264	0·219	0·171	0·145	0·118	0·062	0
k_H/k_D	1·23	1·25	1·31	1·36	1·30	1·24	1·21

Each constant is the mean of three independent determinations; the reproducibility being better than 1%. The uncertainty of k_H/k_D is at most 0·02.

state is far from being, in this solvent, a "true" carbonium ion.

(*b*) The position of the maximum, which is around 95% alcohol in ethanol–water mixtures, will depend upon the nature of the alcohol; methanol being more "ionizing" than ethanol, the maximum will probably be shifted, in this solvent, towards mixtures of lower wâter content; n-propanol being less "ionizing" than ethanol, the maximum will be shifted in the other direction.

(*c*) It is known that the value of the Hammett's ρ-coefficient for a solvolysis decreases as the amount of positive charges on the carbon adjacent to the benzene ring increases; thus a sharp decrease of the Hammett's coefficient with the lowering of the water content of the solvent can be foreseen.

The authors thank Dr. J. Wylde, Chargé de Recherche au C.N.R.S., for many helpful discussions.

(*Received, July* 10*th*, 1967; *Com.* 710.)

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