The Nature of the Carbanion formed in the Hydrolysis of Phosphonium Salts

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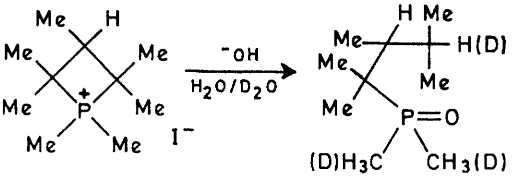
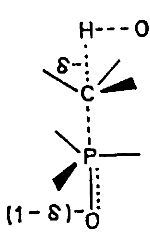
Summary Kinetic isotope effects, k_H/k_D, of *ca.* 1·2 observed in the protonation of carbanions formed in phosphonium salt hydrolysis show that these carbanions are not free in the rate-determining transition state.

THE alkaline hydrolysis of phosphonium salts involves, in the rate-determining step, expulsion of that group most stable as the anion which is protonated to give the corresponding hydrocarbon. Alexander, Eaborn, and Traylor[1] have recently shown that in the similar hydrolysis of silicon and tin compounds the expelled anions are not completely free but are being protonated as formed, kinetic isotope effects, k_H/k_D, of 1·4—4·6 being observed for this step when the reactions were carried out in MeOH–MeOD (1 : 1). We now report on the kinetic isotope effects observed when phosphonium salts are hydrolysed in H_2O–D_2O (1 : 1).



(I) (II)

Because of the rapid exchange of α-hydrogens in alkaline solution only phosphonium salts without such hydrogens could be used. Analysis by mass spectrometry† of the benzene fraction produced from tetraphenylphosphonium iodide showed $k_H/k_D = 1{\cdot}22 \pm 0{\cdot}05$ for protonation–deuteriation of the phenyl anion. Similar analysis of the cumenes‡ from hydrolysis of cumyltriphenylphosphonium iodide showed $k_H/k_D = 1{\cdot}21 \pm 0{\cdot}05$ for protonation–deuteriation of the cumyl anion§ and integration of the n.m.r. spectrum of the cumenes gave a comparable although less accurate figure. Comparison of the n.m.r. spectrum of the oxides (II) formed on hydrolysis of the phosphetanium salt (I) in H_2O–D_2O (1 : 1) with known mixtures of the oxides produced in water and in deuterium oxide gave $k_H/k_D = 1{\cdot}1 \pm 0{\cdot}1$.



(III)

The low kinetic isotope effects observed agree with a picture of phosphonium salt hydrolysis in which in the transition state (III) of the rate-determining step little breaking of the phosphorus–carbon bond has occurred and there is correspondingly little transfer of a proton to the incipient carbanion. The observed[2] overall kinetic isotope effect for the hydrolysis of benzyltriphenylphosphonium bromide in 75% ethanol of $k_H/k_D = 0{\cdot}6$, the relatively small difference (*ca.* 100×) between the rates of hydrolysis of comparable benzyl- and phenyl-phosphonium salts,[3] and the small partial rate factors for loss of *p*-substituted benzyls[4] support this view.

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† At an ionising potential of 14 ev to avoid (M — 1) fragments.

‡ The cumenes were separated from an approximately equal quantity of α-methylstyrene, formed by Hofmann elimination, by preparative g.l.c., fractionation of the cumenes being avoided.

§ The cumyl anion of cumylpotassium does not differentiate between water and deuterium oxide.

[1] R. Alexander, C. Eaborn, and T. G. Traylor, *J. Organometallic Chem.*, 1970, **21**, *P*65.
[2] N. J. De'ath and S. Trippett, unpublished data.
[3] *E.g.*, G. Aksnes and J. Songstad, *Acta Chem. Scand.*, 1962, **16**, 1426.
[4] M. Zanger, C. A. VanderWerf, and W. E. McEwen, *J. Amer. Chem. Soc.*, 1959, **81**, 3806.