Kinetics of Alkaline Hydrolysis of Quaternary Phosphonium Salts. The Influence of Aprotic Solvents on the Hydrolysis of Ethyl(phenyl)phosphonium Iodides

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Third-order rate constants have been determined for the hydrolyses of the ethyl(phenyl)phosphonium iodides (1) in aqueous methanol and in aqueous tetrahydrofuran. The very large increase in the rate of hydrolysis of tetra- and tri-arylphosphonium salts which is induced by the addition of tetrahydrofuran to the medium drops to almost zero for tetra- and tri-alkylphosphonium salts. This is attributed to an increase in the delocalisation of the positive charge in phosphorus, which leads to less specific solvation of the alkylphosphonium ions.

The rates of alkaline hydrolysis of tetraphenylphosphonium chloride [1] and triphenylbenzylphosphonium bromide [2] increase dramatically upon the substitution of most of the water in the medium by an aprotic solvent such as tetrahydrofuran (THF). The effect is also responsible for the very marked hydrolytic sensitivity of ether solutions of phosphonium ylides.[2] Much smaller increases of rate occur when alcohol is added to the aqueous medium.[3]

The rates of hydrolysis of quaternary phosphonium salts in aqueous alcohol media decrease as alkyl groups replace aryl groups bound to phosphorus. The rates are so slow for tetra-alkylphosphonium salts that it is difficult to obtain accurate kinetic data.[4] It has been shown that for aqueous ethanol media the rates of hydrolysis of methyltriphenyl-, dimethyldiphenyl-, and trimethylphenyl-phosphonium salts vary inversely as the dielectric constant of the medium.[5] Thus the much larger changes in the dielectric constant of the solvent produced by the addition of aprotic solvents such as THF appear to offer a means of achieving much larger rate enhancements for the hydrolysis of alkylphosphonium salts. The present paper concerns a study of the kinetics of alkaline hydrolysis of a series of ethyl(phenyl)phosphonium iodides (1) in which the number of ethyl groups may vary from 0 to 4.

$$\mathrm{Et}_n\overset{+}{\mathrm{P}}\mathrm{Ph}_{4-n}\mathrm{I}^-$$

(1)

Results

For comparative purposes the rates of hydrolyses of the salts (1; n = 0—4) were recorded using two solvent systems, one of high dielectric constant (70% v/v methanol in water, ε 40)[6] and one of low dielectric constant (70% v/v THF in water, ε 20).[6] In these media the reactants and products remained in solution throughout the reactions thus avoiding the catalytic effects which occur when phosphine oxides are precipitated.[1] The Table gives the third-order rate constants k obtained from linear plots of $1/c_t^2 - 1/c_0^2$ against time. The reactions were normally followed to 80% completion. The temperature for the hydrolyses in aqueous methanol was raised to 55 °C in order to obtain plots with acceptable correlation coefficients for the whole series. The Table shows the change in the rate enhancement induced by the change in the dielectric constant of the medium, where R_p is the ratio of the rate constants for the two solvent systems [see equation (1)]. The data have not been adjusted

$$R_p = \frac{k\ \text{(aqueous THF media)}}{k\ \text{(aqueous methanol media)}} \qquad (1)$$

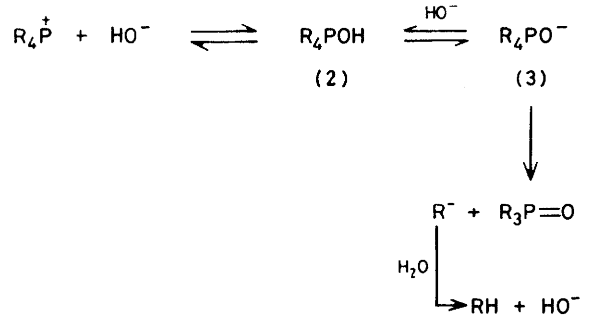
for the difference in temperature of the two media. The Table shows that for both media the third-order rate constant decreases as the number of ethyl groups bound to phosphorus increases. Also, as expected, the rate constants are larger for hydrolyses in aqueous THF medium than in aqueous methanol. However, it was surprising to find that the rate enhancement produced by the presence of THF varied greatly for different salts. The Table shows the huge decrease in the rate enhancement as the aliphatic character of the phosphonium salt increases. The ratio, R_p, which quantifies this effect falls from 770 for tetraphenylphosphonium iodide to only 1.5 for tetraethylphosphonium iodide.

Table. Third-order rate constants k for ethyl(phenyl)phosphonium iodides (1) in aqueous methanol and aqueous THF

	Rate constants k/dm^6 mol^{-2} min^{-1}		
Compound	70% v/v methanol in water at 50 °C	70% v/v THF in water at 40 °C	R_p
(1; n = 0)	8.13×10^{-1}	6.25×10^{2}	770
(1; n = 1)	2.30×10^{-1}	3.71×10	161
(1; n = 2)	1.20×10^{-1}	2.20	18.3
(1; n = 3)	6.0×10^{-2}	1.20×10^{-1}	2.0
(1; n = 4)	4.82×10^{-2}	7.20×10^{-2}	1.5

Discussion

The mechanism of the alkaline hydrolysis of quaternary phosphonium salts is widely accepted to be normally that shown in the Scheme. There are two further conclusions which relate directly to the results presented here. First, the decrease in rate of hydrolysis of quaternary phosphonium salts as the aliphatic character of the salt increases has been attributed to the greater electron-releasing power of the alkyl groups. Induction and hyperconjugation delocalise the positive charge on phosphorus and decrease the availability of the d orbitals which are required for the formation of the hydroxyphosphorane intermediate (2).[5] Second, kinetic and thermodynamic data support the view that the enhancement in rate produced by the addition of aprotic solvents is due to the desolvation of the reactants and an increase in the solvation of the hydroxyphosphorane intermediate (2).[1]



Scheme. Mechanism of alkaline hydrolysis of quaternary phosphonium salts

The present results may be explained within the main points of the above conclusions if the reasonable assumption is made that the effect of changing the solvating power of the medium will be least when there is most dispersion of the charge. Thus, if the positive charge resides largely on the phosphorus atom of arylphosphonium salts, possibly stabilised to some extent by d_π–p_π bonding, the salt will have a strongly bound shell of solvent molecules in which water molecules co-ordinated to the phosphorus atom play a vital role. The addition of an aprotic solvent competes for the water and destabilises the solvent structure surrounding the phosphorus atom. Consequently the energy of the reactants is raised and the pre-equilibrium altered in favour of the hydroxyphosphorane intermediate.

The delocalisation of the positive charge envisaged for the aliphatic salts will lead to a more loose and less specific solvent shell and the above effects will be reduced. Nevertheless, the smallness of the effect for aliphatic salts is most remarkable and the operation of a compensatory effect should be considered. Such an effect has been observed for tetraphenylphosphonium chloride where the addition of dipolar solvents produces a decrease in the frequency factor and entropy of activation which partly compensate the dominant drop in the activation energy.[1] We do not know whether this is an effect on another part of the mechanism, such as the reorganisation of the solvent structure about the oxy-anion (3) and/or the hydroxide ion, but it seems likely that for the alkylphosphonium salts it is nearly balancing the solvent changes at the phosphonium centre.

It has been known for a long time that the addition of slow-reacting arylphosphonium salts and arylarsonium salts accelerates the rates of hydrolysis.[7] Phosphine oxides and aliphatic salts have a much smaller effect. Charge-transfer complexes between aryl rings have been invoked as a possible reason for these observations.[8] However, from the results presented in this paper it is possible that the aryl salts may be acting like the aprotic solvents and simply competing with the hydrolysing salt for the solvation thus destabilising the solvent structure at the reacting phosphonium centre.

A factor which has not been considered with regard to the hydrolyses of the ethyl(phenyl)phosphonium salts is the change in the nature or number of leaving groups.[9] Whilst at least one phenyl group is bound to phosphorus, the expelled group will always be the phenyl anion. Thus, a reduction in the number of phenyl groups will reduce the rate of hydrolysis for statistical reasons; also for tetraethylphosphonium iodide the leaving group is different. However, the comparative nature of the study should ensure that the major influence of changes in the leaving groups should cancel out. Work is in progress to confirm this assumption.

Experimental

Phosphonium Iodides.—The salts (1; $n = 1$—4) were prepared from ethyl iodide and the appropriate phosphine. They were purified by recrystallisation from trichloromethane–ether mixtures except for the salt (1; $n = 1$) which was recrystallised from water. Tetraphenylphosphonium iodide was prepared and purified by the method of Chatt and Mann.[10] The phosphines (apart from triphenylphosphine which was purchased) were prepared by the method of Davies and Jones.[11] The purity of the salts was established by ^{1}H and ^{31}P n.m.r. spectroscopy, and by comparison of the m.p.s with published data.

Kinetics of Alkaline Hydrolysis.—Apparatus. Class B volumetric pipettes and burettes were employed. Equilibration of solutions and the kinetic runs were carried out in a thermostatted water-bath which was covered with small polystyrene spheres and agitated by a circotherm apparatus. The bath temperature was recorded by a 6 cm immersion Griffin and George thermometer, −5 to 105 °C in steps of 0.1 °C.

(a) Titre and quench reagents. Volucon hydrochloric acid and sodium hydroxide standards were used for quench and titre respectively throughout the project. Hydrochloric acid (25.0 cm^3, 0.1M) was made up to 1 000 cm^3 (0.0025M) and NaOH (25 cm^3, 0.1M) made up to 2 000 cm^3 (0.001 25M).

(b) 0.05M-Sodium hydroxide in aqueous organic mixtures. Sodium hydroxide pellets (0.10 g) were dissolved in water (15.0 cm^3) to which organic solvent (35.0 cm^3) was added to produce 0.05M-NaOH in 70% organic solvent–30% water medium.

(c) Phosphonium salt solutions. An appropriate weight of the phosphonium salt was dissolved in the solvent mixtures to produce a 0.05M solution of the salt.

Procedure (a) Back-titration method. An exact volume of sodium hydroxide solution was dispensed in a reaction vessel and equilibrated at a predetermined temperature in the water-bath. An equivalent volume of the phosphonium salt solution, which had also been equilibrated at the same temperature, was dispensed from the same pipette (having been washed and dried) into the reaction vessel, which was immediately sealed (with rubber or Teflon stopper), and mixed. The method of mixing depended on the type of reaction and the general rate of hydrolysis. The faster reactions were carried out in a 100 cm^3 tall-form beaker equipped with a rubber stopper, with provision for a mechanical stirrer and for removal of portions. The slower reactions were carried out in a single flask stoppered with Teflon from which portions were removed, or, alternatively, in identical smaller flasks stoppered with Teflon and in which case the entire content was quenched with standard 0.0025M-HCl. The latter procedure eliminates errors due to evaporation of the volatile component of the solvent system. Where Teflon stoppers were used, the flasks were vigorously shaken before samples were quenched and back-titrated. A capillary pipette was used to withdraw 1.0 cm^3 of the well mixed reaction mixture and added to the quench solution.

The time at which a particular portion or sample was quenched was taken to be the average of the time at which the portion started to flow into the quenching solution and the time at which the portion stopped flowing. The opening from which the portion was taken was sealed as soon as possible after each sampling. The quenched sample was back-titrated with 0.001 25M-NaOH solution and the end-point determined by pH meter. The final titration reading was taken at pH 6.

Errors. Systematic errors due to the interaction between the sodium hydroxide and atmospheric carbon dioxide were minimised by exposing the solutions to air only when absolutely necessary. The sodium hydroxide was standardised prior to each kinetic run. The error in the titres was probably ±0.05 cm^3 which, although small, would have an appreciable effect on the lower titre values. Other random errors were estimated to be: pH meter reading 1%, sampling 1%, and temperature ±0.1 °C. The graphical evaluation of the rate constants from the slopes of the third-order plots was possibly the largest source of error (*ca.* 5%) and the quoted rate constants are thought likely to be accurate to ±5—10%.

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