The Mechanism of Hydrolysis of Phosphonium Ylides

By **Andrew Schnell, J. Graham Dawber,** and **John C. Tebby,*** Department of Chemistry, North Staffordshire Polytechnic, Stoke-on-Trent ST4 2DE

The mechanism of hydrolysis of benzylidenetriphenylphosphorane is similar to that of the hydrolysis of the corresponding salt. The much faster rate of hydrolysis of the ylide is due to the different media in which hydrolysis occurs. It has been found that a large reduction in the water content of the media can accelerate the reaction by a factor of $>10^5$. It is proposed that the low polarities of the solutions in which ylides are usually hydrolysed shift the pre-equilibrium concentrations extensively away from phosphonium hydroxide and towards the five co-ordinate hydroxyphosphorane which decomposes under the catalytic action of base to give phosphine oxide and hydrocarbon. The rate of hydrolysis of benzyltriphenylphosphonium bromide is also greatly accelerated in media of low polarity, the rate being similar to that of the ylide in the same media.

THE mechanism of hydrolysis of phosphonium ylides has been assumed to be similar to the mechanism of hydrolysis of quaternary phosphonium salts, *i.e.* proceeding *via* phosphonium hydroxide.[1] This explanation is supported by the isolation of the same phosphine oxides and hydrocarbons as were obtained from the hydrolysis of the corresponding salts.[2] However, the mechanism does not appear to explain several differences between ylide and salt hydrolyses. The ylides are far more sensitive to hydrolysis than are the corresponding salts; phosphonium hydroxides are not normally isolated when water is added to reactive ylides derived from salts with poor leaving groups; and the reactive ylides are hydrolysed more rapidly than stabilised ylides derived from salts with good leaving groups.

In an attempt to explain these differences, we have studied the hydrolysis of benzylidenetriphenylphosphorane (1) and its corresponding phosphonium bromide (2). To compare the rates of hydrolysis in the same media, aqueous tetrahydrofuran mixtures were chosen since the bromide (2) was moderately soluble in this media and the ylide (1) could be prepared in tetrahydrofuran and mixed with water or aqueous tetrahydrofuran to effect hydrolysis in the same media.

When an equal volume of water was mixed with a

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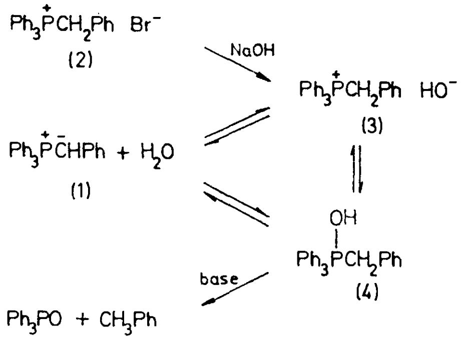
[1] U. Schollkopf, *Angew. Chem.*, 1959, **71**, 260; H. J. Bestmann, *Angew. Chem. Internat. Edn.*, 1965, 4, 583.

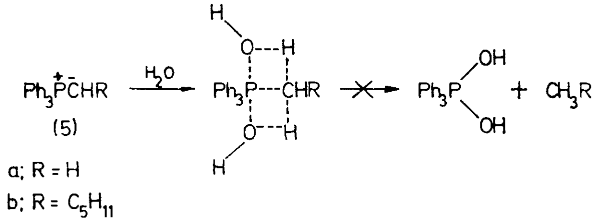
[2] D. Coffman and C. S. Marvel, *J. Amer. Chem. Soc.*, 1929, **51**, 3496; D. Seyferth and G. Singh, *ibid.*, 1965, **87**, 4156; H. J. Bestmann, H. Haberlein, and I. Pils, *Tetrahedron*, 1964, **20**, 2079.

0.025M solution of the ylide (1) in tetrahydrofuran there was an immediate decolourisation of the bright red solution. The mixture was quenched within 5 s in an excess of hydrogen chloride in tetrahydrofuran. Evaporation gave pure triphenylphosphine oxide. A shorter reaction time (1.4 s) was achieved by the continuous flow method. The quenched reaction mixture contained the theoretical yield of toluene and no phosphonium salt. In contrast, toluene formation proceeded slowly in the alkaline hydrolysis of the bromide (2) at the same initial concentration in 50% aqueous tetrahydrofuran; the reaction had a half-life of 450 s.



SCHEME

The large difference in the rate of hydrolysis of the ylide and the salt in these experiments suggested that there was either a drastic change in the relative magnitudes of one or more of the steps in the mechanism or that a different mechanism was operating. A one step mechanism for the ylide hydrolysis which involved concerted PO and CH bond formation was ruled out when hydrolysis of the ylides (5a and b) gave benzene and the corresponding diphenylalkylphosphine oxide.



Solvent effects, known to have an influence on the kinetics,[3] were then examined for the alkaline hydrolysis of the salt (2). A very powerful solvent effect was observed for the hydrolyses in aqueous tetrahydrofuran media (see Table 1); in fact the rates of hydrolysis in media containing <30% water were too fast to measure by conventional back titration and conductimetric procedures. However a transitory yellow colour of the ylide (1) was noted in these very fast reactions. This showed that in media of low polarity there is a considerable shift in the pre-equilibria of the hydrolysis (see Scheme), away from the ionic phosphonium hydroxide (3), and towards the less polar ylide (1) and, by inference, towards the low polarity hydroxyphosphorane (4) as well. It was realised at this stage of the study, that the solvent effect could account for the rapid hydrolysis of the ylide if the mixing of the water and ylide solution in tetrahydrofuran was slower than the rate of hydrolysis of the ylide. Thus the speed and efficiency of mixing could determine the rate of hydrolysis since the ylide, initially in anhydrous tetrahydrofuran, may come into contact with sufficient water to effect complete protonation and then hydrolyse extremely rapidly before the polarity of the medium increases to that corresponding to 50% aqueous tetrahydrofuran.[4]

TABLE 1

Rate data for the alkaline hydrolysis of benzyltriphenylphosphonium bromide (0.025M) with one equivalent of alkali at 22.0°, determined by back-titration and conductimetric methods

% Water v/v	$t_{\frac{1}{2}}$/s	k_3/dm^6 mol^{-2} s^{-1}
60	3 000	0.985
50	450	4.92
40	150	18.75
30	24	73.33

This hypothesis was substantiated by very rapid mixing of water with a solution of the ylide (1) and quenching the reaction mixture in acid at known intervals. The toluene production now was very similar to that given by the conjugate salt (2) at the same concentrations in 50% aqueous tetrahydrofuran. The rate of hydrolysis of the ylide (1) in a number of aqueous tetrahydrofuran mixtures was determined in this way and showed (see Table 2) a similar solvent effect to that of the corresponding salt (2) (Table 1).

TABLE 2

Rate data for the hydrolysis of benzylidenetriphenylphosphorane (0.014M) in aqueous tetrahydrofuran determined by the estimation of toluene using quantitative g.l.c.

% Water v/v	Temp./°C	$t_{\frac{1}{2}}$/s
50	24.2	300
40	24.2	45
30	21.5	9.3
20	22.4	<0.5
10[a]	21.5	<0.02
1	21.5	2.2

[a] The hydrolysis in tetrahydrofuran containing 10% water was complete within the time of mixing (20 ms).

Table 2 shows that the rate of hydrolysis increased as the water content of the medium was reduced and reached a maximum rate at 10% water content. When the water content was further reduced the disappearance of the ylide colouration was not immediate and the reaction could also be followed by the stopped-flow technique. The rate data for the hydrolysis of the ylide under these conditions is summarised in Table 3. Comparison of the two methods used to follow the hydrolysis in 1% aqueous tetrahydrofuran indicated that the g.l.c. method probably under-estimated the half-life by

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[3] H. Hoffmann, *Annalen*, 1960, **634**, 1; G. Aksnes and J. Songstad, *Acta Chem. Scand.*, 1962, **16**, 1426; F. Y. Khalil and G. Aksnes, *ibid.*, 1973, **27**, 3832.

[4] A. Schnell and J. C. Tebby, *J.C.S. Chem. Comm.*, 1975, 134.

a factor of 0.3, since a back titration experiment gave a half-life for this reaction to within 0.1 s of that obtained by the stopped-flow method. Thus the rate of formation of products is very close to the rate of disappearance of ylide. This is in accordance with the existence of a set of pre-equilibria as shown in the Scheme and which will normally include the conjugate base of (4).

TABLE 3

Rate data for the hydrolysis of benzylidenetriphenylphosphorane (0.010M) at 23° determined by the stopped-flow method. $t_{\frac{1}{2}}$ and $t_{\frac{1}{4}}$ are the times for the ylide concentration to be reduced from 0.010M to 0.005 and 0.0025M respectively

% Water v/v	$t_{\frac{1}{2}}$/s	$t_{\frac{1}{4}}$/s	k_2/dm^3 mol^{-1} s^{-1}
1	3.2	7.6	35.3
2	2.1	5.1	53.2
4	0.55	1.55	187.4

Quantitative g.l.c. analysis of the hydrolysis in 1% aqueous tetrahydrofuran shows that the toluene formation and hence the disappearance of ylide follows second-order kinetics * (k_2 32.5 dm^3 mol^{-2} s^{-1}). The stopped-flow method, which was used to measure the time intervals ($t_{\frac{1}{2}}$ and $t_{\frac{1}{4}}$) for the disappearance of ylide, indicates that the reaction order is greater than first with respect to ylide. For a first-order reaction in ylide $t_{\frac{1}{4}}$ should be double the value of $t_{\frac{1}{2}}$, and for a second-order reaction $t_{\frac{1}{4}}$ should be three times the value of $t_{\frac{1}{2}}$. Table 3 shows that the reaction approaches second-order dependence in ylide. The average second-order rate constant, calculated from the stopped-flow data for the hydrolysis in 1% aqueous tetrahydrofuran was 35.3 dm^3 mol^{-1} s^{-1} which is in reasonable agreement with the above value. The second-order dependence upon the ylide concentration could be explained by its involvement as a base catalyst in the decomposition of the hydroxyphosphorane (4), in addition to its participation as a reactant. However the ylide, by its reaction with water, is in equilibrium with hydroxide ion which would be expected to be a very efficient base catalyst. Hydroxide ion may therefore be partly or wholly responsible for the second-order dependence of the rate on the concentration of ylide. The decrease in the rate of hydrolysis as the water content is reduced below 10%, could therefore be due (*a*) to the reduced availability of water as a reactant, and (*b*) to a marked reduction in the concentration of hydroxide ion, which could eventually become so small that attack of hydroxide ion on the hydroxyphosphorane (4) becomes the rate limiting step.

The hydrolysis in 1—4% aqueous tetrahydrofuran was catalysed by aliphatic tertiary amines. Table 4 gives the rates of disappearance of ylide in the presence of triethylamine. The catalytic effect appears to be due to an increase in the concentration of hydroxide ion, from an amine–water interaction, rather than to the amine itself acting as a general base. This conclusion is based on the small increase in rate relative to the amount of amine added and on the relegation of ylide to first-order dependence (as shown by the successive values of $t_{\frac{1}{2}}$ and $t_{\frac{1}{4}}$ in Table 4) when a large excess (100 equiv.) of amine was present.

TABLE 4

Rate data for the hydrolysis of benzylidenetriphenylphosphorane (0.010M) in the presence of triethylamine at 23° determined by the stopped-flow method

% Water v/v	Mole ratio triethylamine : ylide	$t_{\frac{1}{2}}$/s	$t_{\frac{1}{4}}$/s
1	1	2.3	5.0
1	10	1.7	4.1
1	100	1.0	2.0
2	1	1.4	3.3
2	10	1.0	2.4
2	100	0.6	1.2
4	1	0.55	1.25
4	10	0.4	1.02
4	100	0.28	0.56

In conclusion the very large increase in the rate of hydrolysis as the ether content of the medium is raised, is attributed to a displacement of the pre-equilibria towards the hydroxyphosphorane at the expense of phosphonium hydroxide and also to an increase of the catalytic effect of the hydroxide ion. Both changes are seen as arising from increases in the activity coefficients of the ionic species as the polarity of the medium is reduced. We would also expect there to be an increasing amount of hydroxyphosphorane (4) formed directly from the reaction of ylide and water as the polarity of the medium is reduced.

EXPERIMENTAL

All procedures involving solutions of the ylide were carried out under oxygen-free dry nitrogen.

Benzyltriphenylphosphonium Bromide (2).—To a stirred solution of triphenylphosphine (26.2 g, 0.1 mol) in toluene (100 ml) was added dropwise benzyl bromide (17.1 g, 0.1 mol). After 1 h reflux the salt began to precipitate. The mixture was kept just below boiling for 3 h before cooling and filtering. The salt, which was washed with toluene and recrystallised from hot water or chloroform–ether, had m.p. 292° (lit.,[5] 288°).

Benzylidenetriphenylphosphorane (1).—A suspension of dry finely powdered bromide (2) (10.8 g, 0.025 mol) in dry tetrahydrofuran † (200 ml) was treated with powdered sodium hydride (0.75 g) with stirring for 18 h at room temperature.[6] The sodium bromide and unchanged sodium hydride were allowed to settle and the clear supernatant red solution decanted through a glass tube, using positive nitrogen pressure, into sealed bottles equipped with pressure outlet tubes. The solutions were estimated by quenching into a known excess of standard aqueous hydrochloric acid and back-titrating with alkali.

Solutions of ylide (1) prepared in this manner invariably contained toluene from hydrolysis during the preparation. Solutions of the ylide free of toluene were prepared by

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* First-order plots were non-linear.

† Tetrahydrofuran was distilled from sodium, refluxed with lithium aluminium hydride for 18 h, and then distilled into the reaction flask. Dry tetrahydrofuran was also obtained by distillation from solutions of benzylidenetriphenylphosphorane.

[5] G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 1929, 2342.

[6] H. Schmidbauer, H. Stuhler, and W. Vornberger, *Chem. Ber.*, 1972, **105**, 1084.

generating ylide above its maximum solubility in tetrahydrofuran (0.12M), *e.g.* as above but using 50 ml tetrahydrofuran. After the ylide had precipitated the supernatant solution was decanted, as described above, and dry tetrahydrofuran distilled into the flask containing the precipitated ylide. After stirring, the pure solution of ylide was decanted into dry graduated flasks with Teflon stoppers. The solutions could be stored for several weeks in these flasks without appreciable deterioration.

Kinetics of Phosphonium Salt Hydrolysis.—(a) *Back titration method.* Equimolar solutions (usually 20.0 ml of *ca.* 0.05M) of the bromide (2) and sodium hydroxide in the appropriate mixture of aqueous tetrahydrofuran were equilibrated in a thermostatted bath (±0.1°). The reactions were started by mixing the solutions in a 50 ml tall-form beaker equipped with a rubber top, with provision for a stirrer and for the removal of aliquot portions. The portions (1 or 2 ml) were quenched in an excess of standardised dilute hydrochloric acid and back-titrated against alkali using Bromothymol Blue.

(b) *Conductimetric method.* The reaction beaker described above was equipped with a stirrer and conductivity electrodes (3 × 5 mm platinum). The equilibrated solutions, as in (a), were quickly mixed and the decrease in conductivity monitored using a Wayne–Kerr autobalance conductivity bridge (model 641 B). The results were evaluated in the manner suggested by Allen.[7] The reading at the time of mixing did not correspond to that estimated from the addition of the conductivities (measured separately) of the reactants at half the concentration. This value is important for the calculation of the concentration of phosphonium hydroxide. Generally the conductivity read from the bridge at the time of mixing gave the best agreement with the kinetics estimated by method (a). The reactions were followed to 70% completion. The order of the reaction was evaluated by the method of integration, and confirmed third-order kinetics, as reported by other workers.[3,7,8] The rate data are given in the text.

Kinetics of Ylide Hydrolysis estimated by Continuous Flow Method.—A solution of the ylide (1) in tetrahydrofuran (0.032M) was mixed with an equal volume of water at the head of a gravity feed tube (240 mm in length, 2 mm internal diameter). A flow-rate of 0.9 ml s^{-1} (usually 4.5 ml in 5 s) gave an average reaction time of 1.4 s. The reaction mixture leaving the tube was immediately quenched by hydrogen chloride in tetrahydrofuran. G.l.c. (Carbowax at 105°), using *m*-xylene as standard, showed that the theoretical amount of toluene was produced. The standards also required the presence of similar concentrations of hydrogen chloride and water in order to obtain an accurate analysis. T.l.c. showed the presence of phosphine oxide and no phosphonium salt.

Kinetics of Ylide Hydrolysis with Rapid Mixing.—(a) *G.l.c. method.* A solution of the ylide (1) in tetrahydrofuran (0.028M) was rapidly mixed * with an equal volume of water or aqueous tetrahydrofuran and allowed to react in a separate vessel for a known time before quenching with excess of hydrogen chloride in tetrahydrofuran. The toluene was estimated by g.l.c. as described above and in several runs the phosphonium hydroxide was estimated by back-titration.

(b) *Stopped flow method.*[9] A Nortech SF1A stopped-flow spectrometer was used, which mixed the reactants in *ca.* 20 ms. The concentration of ylide, which absorbed light in the region of 500 nm, was monitored by feeding the output from the photocell into a storage oscilloscope. The optical density of the ylide solution in the 500 nm region varied non-linearly with concentration and therefore the oscilloscope trace was calibrated directly from standard solutions of the ylide. These solutions were prepared *in situ* by dilutions with equal volumes of super-dry tetrahydrofuran in an all-glass apparatus under a positive pressure of nitrogen. The hydrolyses were carried out at 23° by mixing equal volumes of ylide solution (*ca.* 0.02M in tetrahydrofuran) and 2, 4, or 8 ml aqueous tetrahydrofuran. The times required for the concentration of the ylide to decrease to the values used in the calibration were read directly from the oscilloscope trace. Each experiment was repeated many times and the reaction curves found to be superimposable up to 75% completion of the reaction. The half-lives obtained are given in Table 3. The experiments were repeated with 1, 10, or 100 equiv. triethylamine added to the aqueous tetrahydrofuran. The half-lives are given in Table 4.

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* Mixing within 20 ms was achieved using the mixing device on a stopped-flow apparatus.

[7] D. W. Allen, *J. Chem. Soc.* (*B*), 1970, 1490.

[8] M. Zanger, C. A. VanderWerf, and W. E. McEwen, *J. Amer. Chem. Soc.*, 1959, **81**, 3806.

[9] E. F. Caldin, 'Fast Reactions in Solution,' Blackwell, Oxford, 1964, ch. 3; D. N. Hague, 'Fast Reactions,' Wiley, London, 1971, ch. 2.