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VOLUME PROFILES AND MECHANISMS FOR THE ALKALINE DECOMPOSITION OF PHOSPHONIUM SALTS AND PHOSPHATE ESTERS

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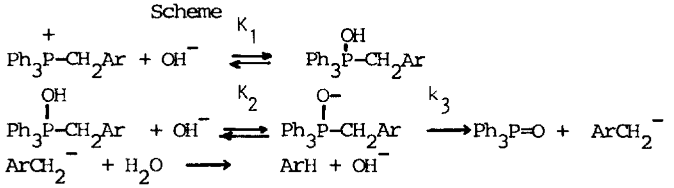
Abstract: Volumes of activation have been measured for the alkaline decomposition of triphenylbenzylphosphonium and triphenyl(p-nitrobenzyl)phosphonium ions which lead to the formation of triphenylphosphine oxide and the toluene.The rates of reaction are very strongly retarded by pressure, volumes of activation are +32 cm^{3}mol^{-1} while the volume of reaction is +16. This accords with a two- or three-step mechanism, involving desolvation and fragmentation each of which contributes an increase in volume. Diethyl(p-nitrophenylphosphate hydrolyses by a $B_{Ac}2$ mechanism, $\Delta V^{\neq}$= -16.

The alkaline hydrolysis of phosphonium salts leads to the formation of the phosphine oxide and hydrocarbon derived from the most stable carbanion which can be expelled. The reaction provides an indirect method for the reduction of alkyl halides.

$$Ar_3\overset{+}{P}\text{-}R \quad + \; OH^- \longrightarrow Ar_3P{=}O + RH$$

Reactions have been found to be of first order in phosphonium ion and normally of second order in hydroxide [1]. Rates are reported to decrease as solvent polarity increases as evidenced by a positive slope of a plot between log k and 1/D [2,3]. When R= $-CH_2Ar$, rates are strongly accelerated by electron-withdrawing substituents, the Hammett reaction constant, ρ ,having values variously determined between +3.2 and +5.6 according to the conditions [4-6]. Rates are also enhanced by electron-withdrawing groups in the aryl ligands which remain attached to phosphorus, ρ = +2.2 to +3.8 [7]. These observations can be accommodated in the mechanism, set out in the Scheme in which initial attachment of OH^- to phosphorus is followed by ionisation of the hydroxyphosphorane and expulsion of a carbanion.The second-order dependence on $[OH^-]$ accords with the necessity for removing a proton from the first intermediate; the reaction constants are in agreement with electron-withdrawing groups favouring the equilibria K_1 and K_2 and especially the rate-determining step k_3. The available evidence ,however, does not support a correlation with σ^- which would be expected if carbanionic character were developing in the leaving group so possibly protonation of carbon occurs synchronously with expulsion of the incipient carbanion.

Scheme



$$Ph_3\overset{+}{P}\text{-}CH_2Ar + OH^- \overset{K_1}{\rightleftharpoons} Ph_3\overset{OH}{P}\text{-}CH_2Ar$$
$$Ph_3\overset{OH}{P}\text{-}CH_2Ar \;+ OH^- \overset{K_2}{\rightleftharpoons} Ph_3\overset{O-}{P}\text{-}CH_2Ar \xrightarrow{k_3} Ph_3P{=}O + ArCH_2^-$$
$$ArCH_2^- \;+ H_2O \longrightarrow ArH + OH^-$$

We have re-examined the kinetics of this reaction and have measured the volume profile by observing the effects of pressure on rates and densities of solutions of all the reactants and products , Table. Measurements on triphenylbenzylphosphonium ion produced third-order rate constants. Those on triphenyl-p-nitrobenzylphosphonium ion were conducted in a bicarbonate buffer, pH = 9.60 (and corrected for the effects of pressure on its pH) so that these are pseudo-first order constants.Rates are found to be strongly depressed by pressure and activation volumes of +32 $cm^3 mol^{-1}$ are found ,some of the largest positive values known.

Table

A. Rates of Hydrolysis of Diethyl p-Nitrophenyl Phosphate at Different Pressures; (in 50% v/v aqueous ethanol, 298 K)

p/bar	10^3 k/min^{-1}	p/bar	10^3k/min^{-1}
1	7.90	600	12.8
200	9.0	800	13.10
400	12.8	1000	14.7

$\Delta V^{\neq}$ = -16 +/- 2 cm^3 mol^{-1}

B. Rates of Alkaline Decomposition of Triphenylbenzylphosphonium Bromide (in 50% v/v aqueous ethanol, 318 K,standard deviation in k,2-3%)

p/bar	$k_3/M^{-2}min^{-2}$	p/bar	$k_3/M^{-2}min^{-2}$
1	47.4	650	23.0
210	38.4	750	21.1
330	34.7	820	20.6
420	31.1	900	18.0
500	28.8	1000	17.2

$\Delta V^{\neq}$ = +31 +/-2 $cm^3 mol^{-1}$

C. Rates of Alkaline Decomposition of Triphenyl(p-nitro)benzylphosphonium Bromide (in 50% v/v aqueous ethanol, 298 K,pH=9.6,standard deviation in k,2-3%)

p/bar	10^3k/min^{-1}	p/bar	10^3k/min^{-1}
1	30.8	400	16.5
100	25.8	500	14.9
200	20.0	600	13.0
300	19.5	800	9.7
		900	8.0

$\Delta V^{\neq}$ = +32 +/- 3; ΔV = + 16 +/- 2 $cm^3 mol^{-1}$

If the mechanism is as described in the scheme, the rate law eq. 1 would apply;

$$\text{rate} = K_1K_2\,k_3\,[Ar_3^+][OH^-]^2 \qquad 1$$

and $\Delta V^{\neq}_{obs} = \Delta V_1 + \Delta V_2 + \Delta V^{\neq}_3$

estimated values +20 0 +10 cm^3mol^{-1}

Pressure would be expected to displace the equilibrium K_1 towards the left,since the negative contribution toΔV_1 due to bond-formation is more than offset by the positive volume change accompanying loss of charge and relaxation of electrostricted solvent . The volume of activation for coordination of OH^- to neutral phosphorus was determined by measurement of the pressure-dependence of rates of phosphate ester hydrolysis. The value of -16 cm^3mol^1 obtained is very similar to that of $B_{Ac}2$ carboxylic ester hydrolyses and presumably reflects a common mechanism. The proton transfer between two oxygen bases, K_2 would be insensitive to pressure while the rate-determining step k_3 would contribute a positive volume change due to bond fission and possibly also charge delocalisation. The large positive value of $\Delta V^{\neq}$ observed appears therefore to be in accordance with the Scheme.

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