

Kinetic Study of the Reaction between Phosponium Compounds and Hydroxyl respectively Alkoxide Ions

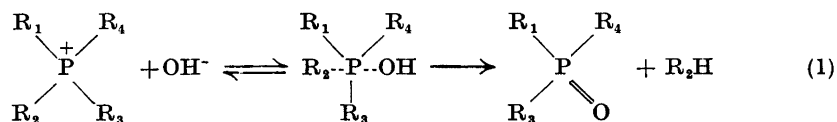
GUNNAR AKSNES and JON SONGSTAD

Chemical Institute, University of Bergen, Bergen, Norway

The alkaline decomposition of quaternary phosphonium compounds in different water-alcohol mixtures was found to obey third or second order kinetics dependent on the stability of the leaving negatively charged organic group. Thus, tetraphenyl and triphenylbenzyl phosphonium hydroxides were decomposed according to third order kinetics, first order dependence on the concentration of phosphonium ions and second order on the hydroxyl ions. This is in agreement with the observations of McEwen and co-workers¹. However, the decomposition of triphenyl-*p*-nitrobenzyl phosphonium hydroxide followed second order kinetics, first order dependence on the concentration of phosphonium ions and first order on the hydroxyl ions. The difference in order is assumed to be due to a greater instability of the pentacovalent intermediate formed when *p*-nitrobenzyl is the leaving group as compared with the intermediates formed from tetraphenyl respectively triphenylbenzyl phosphonium compounds where phenyl respectively benzyl are the leaving groups.

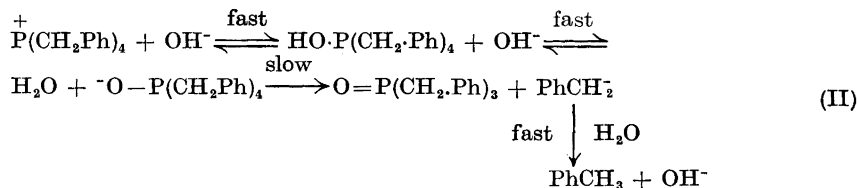
It is shown that the decomposition of tetraphenyl and triphenylbenzyl phosphonium alkoxides obey third order kinetics. However, the dependence of the rate of hydrolysis upon alcohol concentration in the reaction solution, (plot of $\log k$ versus $1/D$) shows that the rate determining step must be different for the hydroxide and alkoxide reactions. The mechanisms of the decomposition of phosphonium compounds by hydroxide as well as alkoxide ions are discussed.

Ingold and co-workers² have postulated that the alkaline decomposition of quaternary phosphonium compounds proceeds through a pentacovalent (trigonal bipyramidal) transition state:

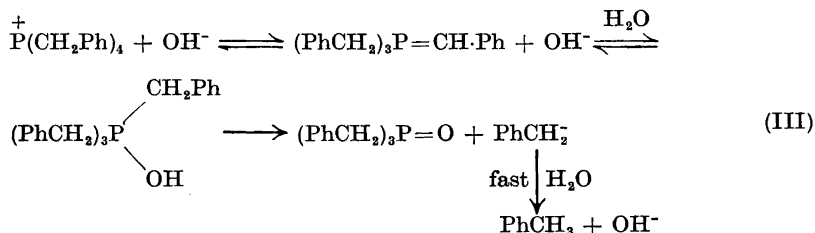


McEwen and co-workers¹ and Hoffman⁷ observed that phosphonium compounds containing benzyl or substituted benzyl groups were decomposed by hydroxyl ions according to third order kinetics, first order dependence on

hydroxyl ion concentration. The benzyl or the substituted benzyl groups were split off as toluene respectively substituted toluenes. The authors explained the decomposition according to the following reaction scheme (tetrabenzyl phosphonium hydroxide as example):



Since it is known that phosphonium compounds containing benzyl or substituted benzyl groups very easily form the corresponding phosphoranes in strongly alkaline solution³, there seemed to exist the possibility that the third order kinetics observed for the alkaline decomposition of benzyl-containing phosphonium compounds might be due to the formation of a phosphorane as an intermediate compound which in turn might be attacked by hydroxyl ions and water to give a pentacovalent transition state:



If the second step in the above scheme is rate determining, the third order kinetics could be accounted for without postulating the decomposition of a pentacovalent intermediate as rate determining step. In order to throw light

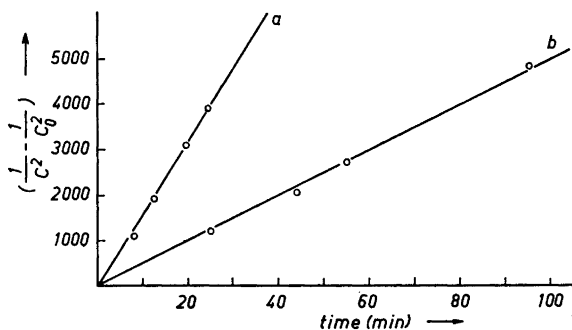


Fig. 1. Hydrolysis of phosphonium hydroxides a) 0.0524 M triphenylbenzyl phosphonium hydroxide in 75 % alcohol-water mixture at 35°C. b) 0.524 M tetraphenyl phosphonium hydroxide in 80 % alcohol-water mixture at 50°C.

on this question we have studied the alkaline decomposition of tetraphenyl, triphenylbenzyl and triphenyl-*p*-nitrobenzyl phosphonium compounds, in different water-alcohol mixtures. The chief differences between the three phosphonium ions are that benzyl- respectively *p*-nitrobenzyl-containing phosphonium cations easily form phosphoranes in alkaline solution whereas this is not the case with tetraphenyl phosphonium ions. It seems therefore safe to conclude that the only reasonable way in which the tetraphenyl phosphonium cation is attacked by hydroxyl ions is through a direct attack of the hydroxyl ion on the phosphorus atom forming a pentacovalent intermediate or transition state. If the tetraphenyl phosphonium ions are decomposed according to third order kinetics, the formation of a pentacovalent intermediate the decomposition of which is rate determining, appears to be the only reasonable explanation.

EXPERIMENTAL

Tetraphenyl phosphonium bromide was synthesized according to descriptions by Dodonow and Medox⁴. (Found: Br 17.50; 17.65. Calc. for $C_{24}H_{20}PBr \cdot 2H_2O$: Br 17.58.)

Triphenylbenzyl phosphonium chloride was made by heating a mixture of equivalent amounts of triphenyl phosphine and benzyl chloride to 120°C for one hour. The crystalline product was recrystallized two times from alcohol-ether mixture. (Found: Cl 9.16; 9.21. Calc for $C_{25}H_{22}PCl$: Cl 9.12.)

*Triphenyl-*p*-nitrobenzyl phosphonium chloride* was synthesized in the same way as the benzyl derivative. The compound was recrystallized two times from alcohol-ether mixture. (Found: Cl 8.16; 8.08. Calc. for $C_{25}H_{20}O_2N PCl$: Cl 8.17.)

Kinetic measurements. The reactions between tetraphenyl and triphenylbenzyl phosphonium halogenides and sodium hydroxide were performed with equivalent amounts of both reactants. The course of reaction was followed by titration of the unreacted hydroxyl ions after fixed intervals of time. The reactions were normally followed until approximately 70 % hydrolysis. However, in the cases where the hydrolysis were studied below 50 % (by volume) of alcohol in the alcohol-water mixture, the rate constants were calculated from the data below 30 % hydrolysis. This was done in order to avoid precipitation of triphenyl phosphine oxide which was found to accelerate greatly the rate of hydrolysis.

The determination of the rate of reaction between triphenyl-*p*-nitrobenzyl phosphonium chloride and hydroxyl ions was performed with the Radiometer Titrator (T.T.T.I.C.) at pH 10.00, 10.30 and 10.60. The phosphonium compound was always in so great excess that the reaction showed zero order rate dependence with respect to this reactant.

RESULTS AND DISCUSSION

In Fig. 1 are recorded two typical runs for the alkaline decomposition of tetraphenyl and triphenylbenzyl phosphonium compounds where the initial concentrations of the reactants are identical. The third order constant is therefore: $k = \frac{1}{2t} \left(\frac{1}{C^2} - \frac{1}{C_0^2} \right)$ where t = time in min, C_0 = initial concentration of phosphonium cations respectively hydroxyl ions and C = concentration at time t . The data show clearly third order rate dependence in accordance with the observation of McEwen and co-workers¹ from their study of decomposition of tetrabenzyl phosphonium hydroxide. Since thus the alkaline decomposition of tetraphenyl phosphonium compounds shows second order rate dependence on the hydroxyl ions in the same way as the benzyl derivatives a mechanism according to reaction scheme III must be ruled out. In agreement

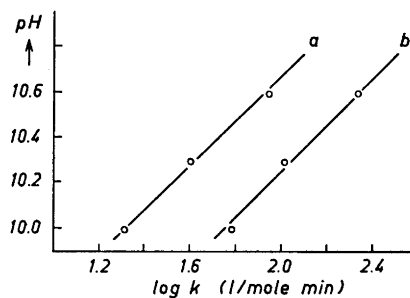


Fig. 2. Plot of $\log k$ against pH for the alkaline decomposition of triphenyl-*p*-nitrobenzyl phosphonium chloride, a) 21°C, b) 31°C.

with McEwen *et al.* we therefore conclude that the reaction between tetraphenyl respectively triphenylbenzyl phosphonium cations and hydroxyl ions involves the formation of a pentacovalent intermediate, the decomposition of which is rate determining for the hydrolysis.

However, the rate determining step is dependent on the substituents linked to phosphorus in the quaternary phosphonium compounds. In Fig. 2

Table 1. Rate constants and activation energies for the alkaline decomposition of tetraphenyl, triphenylbenzyl and triphenyl-*p*-nitrobenzyl phosphonium compounds in alcohol-water mixtures. In all experiments are used equivalent concentrations of hydroxyl ions, resp. alkoxide ions, and phosphonium salt (0.05140 N).

Compound	Volume percent alcohol in reaction solution	Rate constant ($l^2\text{mole}^{-2}\text{min}^{-1}$)				Activation energy E , kcal
		20°C	30°C	40°C	50°C	
Tetraphenyl phosphonium bromide	100	2.75	21.5	—	—	30.8
	95.6	5.28	30.6	—	—	31.0
	80	—	—	5.92	24.4	26.7
	50	—	—	0.184	0.695	26.7
	20	—	—	—	0.085	—
0	—	—	—	0.04	—	
Triphenylbenzyl phosphonium chloride	Volume percent	Rate constant ($l^2\text{mole}^{-2}\text{min}^{-1}$)		E kcal		
		25°C	35°C			
	100	17.8	56.0	21.0		
	75	24.5	79.5	21.5		
	50	4.25	11.2	18.0		
25	—	—3.6	—			
12.5	—	—2.8	—			
0	—	—0.6	—			
Triphenyl- <i>p</i> -nitrobenzyl phosphonium chloride	Volume percent	pH	Rate constant ($l\text{mole}^{-1}\text{min}^{-1}$)		E kcal (average)	
			21°C	31°C		
	50	10.00	20.8	61.8	18.0	
	50	10.30	20.3	56.0		
50	10.60	22.4	56.0			

is plotted $\log k$ against pH for the alkaline decomposition of triphenyl-*p*-nitrobenzyl phosphonium chloride at different fixed pH. The linear dependence shows that in this case the hydrolysis of the phosphonium compound is first order dependent on the hydroxyl ion concentration. We assume that the decomposition of the pentacovalent intermediate containing a *p*-nitrobenzyl group is sufficiently rapid to make the first step in reaction scheme II — the formation of the intermediate — rate determining.

By comparing the activation energies for the alkaline decomposition of the three compounds studied (Table 1) we find that there is a decrease of approximately 10 kcal from the tetraphenyl to the triphenylbenzyl phosphonium compound, in agreement with the easier formation of the negatively charged benzyl ion as compared with the phenyl ion. This observation is in accordance with the qualitative results of Ingold and co-workers² and Horner *et al.*⁵ If the triphenyl-*p*-nitrobenzyl phosphonium compound followed the same kinetics as the tetraphenyl and triphenyl benzyl derivatives one would expect a strong decrease in the activation energy from the benzyl to the *p*-nitrobenzyl derivative due to the strong stabilizing effect of the *p*-nitro group on the benzyl anion. However, the activation energy remains approximately unchanged, which again points to a different kinetic course. The calculated activation energy, 18 kcal, for the decomposition of the *p*-nitrobenzyl compound must therefore be for the formation of the pentacovalent intermediate, whereas the activation energy for the decomposition of the intermediate is expected to lie several kcal lower.

It was observed that on reducing the alcohol content in the reaction solution below a critical value the triphenyl phosphine oxide formed during the reaction began to separate from the solution. The finely divided precipitate

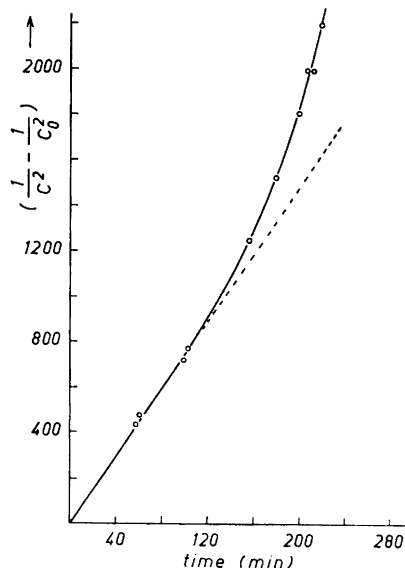


Fig. 3. Hydrolysis of triphenylbenzyl phosphonium hydroxide in 25 % alcohol-water mixture. Concentration 0.0520 M. Temperature 35°C.

of triphenyl phosphine oxide was found to accelerate the rate of hydrolysis. In Fig. 3 is shown a typical experiment for the decomposition of triphenylbenzyl phosphonium hydroxide in 25 % alcohol-water mixture (by volume). As long as the reaction solution keeps the formed phosphine oxide dissolved the rate follows third order kinetics. However, from the moment the separation of the phosphine oxide starts the rate of hydrolysis is greatly increased. We assume that the phosphonium compound is absorbed on the precipitated phosphine oxide thus producing a local high concentration of reactants. If now the reaction with hydroxyl ions take place with the absorbed phosphonium compound the acceleration of the hydrolysis is expected from purely kinetic reasons (*cf.* Hoffmann⁷).

The great increase in the rate of hydrolysis with increasing amount of alcohol in the reaction solution is in accordance with the solvent effect theory. For reactions between two ions the relation between the rate and the dielectric constant of the solution can be expressed in the following way⁶:

$$\ln k = \ln k'_0 - \frac{N \cdot Z_A \cdot Z_B \cdot e^2}{DRT \cdot r^*}$$

where k = calculated rate constant, k'_0 = rate constant in a medium of infinite dielectric constant, N = Avogadro's number, Z_A and Z_B are the charges of the two ions, e = electron charge, D = dielectric constant, R = gas constant, T = absolute temperature and r^* = distance between the ions in the activated complex. The equation predicts a linear plot of $\log k$ against

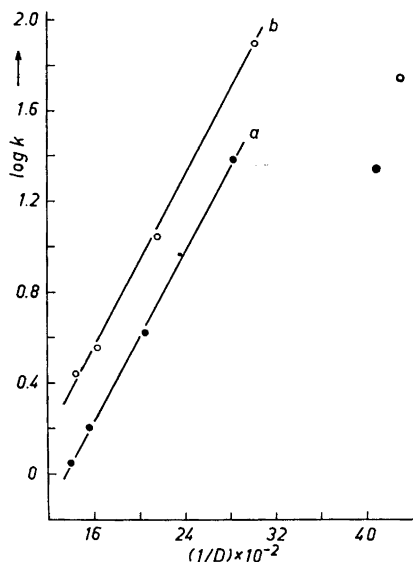


Fig. 4. Plot of $\log k$ against $1/D$ for the decomposition of triphenylbenzyl phosphonium hydroxide a) 25°C b) 35°C.

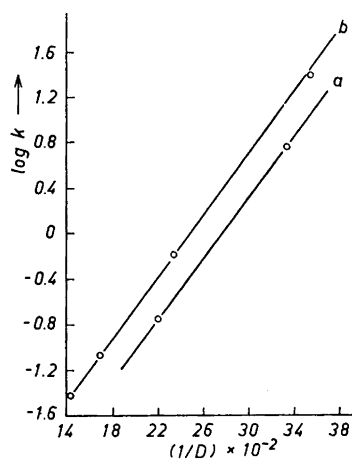
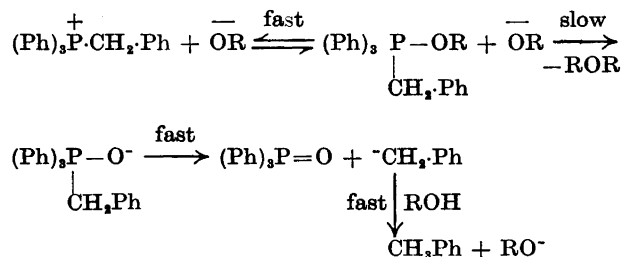


Fig. 5. Plot of $\log k$ against $1/D$ for the decomposition of tetraphenylphosphonium hydroxide a) 40°C b) 50°C.

$1/D$ with a positive slope when the charges of the ions are of opposite sign. In the case of the alkaline decomposition of phosphonium compounds the reaction between the two oppositely charged ions have the character of an equilibrium reaction; the observed rate constant includes the product of the different equilibrium constants and the rate constant of the rate determining step. However, the linear dependence between $\log k$ and $1/D$ should still be valid. In Fig. 4 and 5 is plotted $\log k$ against $1/D$ for the decomposition of triphenylbenzyl and tetraphenyl phosphonium hydroxides. We observe that the values of the rate constants up to 75–80 % alcohol obey the theoretical expression whereas the rates for 100 % alcohol (*i.e.* the rate in pure sodium ethoxide solution) lie far below the predicted values (Fig. 4). Although the rate constants in different alcohol-water mixtures may be influenced through specific solvent effects, not accounted for in the theoretical equation, the observed drastic decrease in the rate in ethoxide solution can only be explained as due to a different reaction mechanism. In reaction scheme II the dissociation of the proton from the pentacovalent intermediate is formulated as a rapid equilibrium reaction; when the alkoxide ion is the reacting base a corresponding rapid equilibrium reaction is not possible, since there is no hydroxyl proton to dissociate. It seems reasonable to expect that step 2 of the following scheme, the nucleophilic reaction between an alkoxide ion and the alkyl group of the pentacovalent intermediate producing ether and a negatively charged intermediate will now be the rate determining step:



This scheme will still give third order rate dependence in accordance with the experimental data. However, the possibility that the second step consists of a nucleophilic attack of alkoxide ion directly on phosphorus in its pentacovalent state should not be overlooked.

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REFERENCES

1. McEwen, W. E., Vander Werf, C. A. and Zander, M. *J. Am. Chem. Soc.* **81** (1959) 3806.
2. Fenton, G. W. and Ingold, C. K. *J. Chem. Soc.* **1929** 2342.
3. Grayson, M. and Keough, P. T. *J. Am. Chem. Soc.* **82** (1960) 3919.
4. Dodonow, J. and Medox, M. *Ber.* **61** (1928) 907.
5. Horner, L., Hoffman, H., Wippel, H. G. and Hassel, G. *Chem. Ber.* **91** (1958) 52.
6. Scatchard, G. *Chem. Revs.* **10** (1932) 229.
7. Hoffmann, H. *Ann.* **634** (1960) 1.

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