Alkaline Decomposition of Methyl Phenyl Phosphonium Compounds

GUNNAR AKSNES and LEIF J. BRUDVIK

Chemical Institute, University of Bergen, Bergen, Norway

The alkaline decomposition of trimethyl phenyl, dimethyl diphenyl, methyl triphenyl and tetraphenyl phosphonium salts has been studied in alcohol-water mixtures. It is found that the rate of decomposition obeyes third order kinetics in alcohol-water mixtures in the region 80-96 % alcohol (by weight). The plot of log k against $1/D$ of the solvent gives a straight line. The alkaline decomposition of methyl phenyl phosphonium salts in absolute alcohol is found to be due to traces of water in the alcohol.

The activation energies and the frequency factors for the alkaline decomposition of the phosphonium compounds are calculated, and are discussed in relation to substituent effects and the $C-H$ stretching frequencies of the methyl groups in the phosphonium salts together with the $P=O$ stretching frequencies of the phosphine oxides formed in the decomposition of the salts.

In a previous paper a kinetic study of the alkaline decomposition of some benzyl and phenyl substituted phosphonium salts was reported [1]. The rate of the decomposition was found to increase strongly with increasing amount of alcohol in the alcohol-water reaction mixture. It was shown that the plot of the logarithm of the rate constant (log k) against the reciprocal of the dielectric constant of the solvent ($1/D$) was linear for mixtures containing from 10 to 80 % of alcohol by volume. In absolute alcohol, however, the rate was found to decrease markedly and it was concluded that this was due to a different reaction mechanism

Parisek *et al.*[2] have shown that the alkaline decomposition of optically active benzyl substituted phosphonium compounds proceeds differently in alkoholic ethoxide solution as compared to alkaline aqueous solution. Further, Grayson and Keough [3] have observed the formation of ether in the decomposition of benzyl substituted phosphonium compounds in alcoholic ethoxide solution. However, no ether formation was detected during decomposition of alkyl phenyl substituted phosphonium salts under corresponding conditions, and Grayson and Keough [3] assumed that the observed decomposition of these salts was due to traces of water in the reaction mixture. In this paper we

report a kinetic study of the alkaline decomposition of some methyl phenyl substituted phosphonium compounds. Our results confirm that alkyl phenyl substituted phosphonium ions are quite stable towards ethoxide ions and that the observed decomposition is caused by traces of water.

EXPERIMENTAL

Dimethyl phenyl phosphine was synthesized from phenyl dichlorophosphine and methyl magnesium bromide in ether solution, b.p.$_8$ 65°C, $n_D^{19.5}$ 1.5673 (Michaelis,[4] b.p.$_{12}$ 74−75°).

Trimethyl phenyl phosphonium bromide was obtained by mixing dimethyl phosphine and methyl bromide in ether solution. Recrystallized from alcohol-ether mixture, m.p. 284−86°C (Found: Br 34.17. Calc. for $C_9H_{14}PBr$: Br 34.30).

Methyl diphenyl phosphine was made from diphenyl chlorophosphine and methyl magnesium bromide in absolute ether, b.p.$_8$ 148°C, $n_D^{19.5}$ 1.6261. (Meisenheimer,[5] b.p^{14}. 161°).

Dimethyl diphenyl phosphonium bromide was made by mixing equivalent amount of methyl bromide and methyl diphenyl phosphine in ether. Recrystallized from alcohol-ether mixture, m.p. 195−96.5°C. (Found: Br 27.01. Calc. for $C_{14}H_{26}PBr$: Br 27.09).

Methyl triphenyl phosphonium bromide was synthesized from methyl bromide and triphenyl phosphine. Recrystallized from alcohol-ether mixture, m.p. 230−32°C (Found: Br 22.25; 22.30. Calc. for $C_{19}H_{18}PBr$: Br 22.38).

Trimethyl phosphine oxide, m.p. 141°C (Fenton and Ingold,[6] m.p. 140−41°), *dimethyl phenyl phosphine oxide*, m.p. 119°C (Meisenheimer,[5] m.p. 100°C), *methyl diphenyl phosphine oxide*, m.p. 113−14°C (Michaelis,[7] m.p. 110−11°) and *triphenyl phosphine* oxide m.p. 157.5°C, were made from the respective phosphonium bromides by treatment with moist silver oxide in water solution. The phosphine oxides were obtained upon evaporation to dryness of the phosphonium hydroxide solution. The first two phosphine oxides were sublimated, whereas the last two were recrystallized from ethyl acetate and thoroughly dried *in vacuo*.

Kinetic measurements. The reactions between the phosphonium salts and sodium hydroxide were performed with equivalent amounts of both reagents (solutions usually approximately 0.05 M in phosphonium bromide and sodium hydroxide). The course of the reaction was followed by titration of the unreacted hydroxyl ions after fixed time intervals. The reaction was followed until approximately 70 % hydrolysis. The third order rate constant were calculated using the formula:

$$k = \frac{1}{2t} \left(\frac{1}{C^2} - \frac{1}{C_0^2} \right)$$

where k = third order rate constant, t = time in minutes, C_0 = initial concentration of phosphonium salt resp. hydroxyl ions, and C = conc. after time t.

The ethoxide solution was made from alcohol which had been distilled with sodium and dried over magnesium.

## MECHANISMS OF THE ALKALINE DECOMPOSITION OF PHOSPHONIUM COMPOUNDS

The alkaline decomposition of methyl phenyl phosphonium compounds was found to obey third order kinetics in alcohol-water mixtures containing from 80 to 96 % alcohol by weight. A typical run is shown in Fig. 1. The experimental data and the calculated third order rate constants in various alcohol-water mixture are recorded in Table 1. For direct comparison of the different rate constants the extrapolated rate values at 80°C are listed in column 9.

Table 1. Rate and thermodynamic data for the alkaline decomposition of methyl phenyl phosphonium bromides.

Compound	Weight % alcohol	Rate constant (l²mole⁻²min⁻¹)						log $k_{80°C}$	Activation energy kcal/mole	Frequency factor log A
		40°C	50°C	60°C	70°C	75°C	80°C			
$\overset{+}{(Me)_3}P.Ph$ Br⁻	74.8	—	—	—	—	0.0828	0.1740	−0.7595	36	21.7
	83 9	—	—	—	—	0.3105	0.6704	−0.1736	37	23.1
	93.4	—	—	—	—	1.673	3.388	0.5299	34.5	21.9
$\overset{+}{(Me)_2}P(Ph)_2$ Br⁻	74.8	—	—	—	2.584	—	10.08	1.0033	32.8	21.3
	83.9	—	—	—	10.61	—	39.57	1.5996	31.7	20.4
	93.4	—	—	12.39	51.54	—	—	2.304	32.4	22.3
$\overset{+}{Me}P(Ph)_3$ Br⁻	74.8	—	2.442	10.58	—	—	—	2.1778	31.4	21.6
	83.9	2.026	9.410	—	—	—	—	2.7436	30.9	21.8
	93.4	10.09	46.41	—	—	—	—	3.4166	30.7	22.4
$\overset{+}{P}(Ph)_4$ Br⁻	93.6	—	—	—	—	—	—	4.3427 *		
	80−95	—	—	—	—	—	—	—	29.3 *	20 *

* Average values calculated from earlier work [1].

The only reaction products observed were benzene and the corresponding phosphine oxides, in agreement with the following mechanism [1,26]:
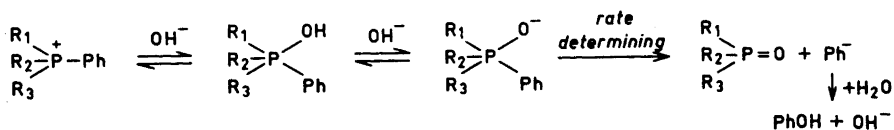
Scheme 1.

where Ph = phenyl, R_1, R_2, and R_3 are phenyl or methyl groups.

Strong evidence that hydroxyl ion is the nucleophile even in alcohol-water mixtures of very low water content is provided by the medium effect. In a previous paper [1] was shown that the plot of log k against $1/D$ for the solvent is linear in alcohol-water mixtures containing between 10 and 80 % alcohol, and it was concluded that hydroxyl ion was the only nucleophile in this concentration range. The present findings show that the linearity of the plot of log $k_{80°C}$ against $1/D$ of the solvent at 80°C persists for alcohol-water mixtures containing at least 96 % of alcohol (Fig. 2). The start concentration of phosphonium compounds in the reaction solution was approximately 0.05 M. Since 96 % alcohol is nearly 2.5 M with respect to water, the concentration of water will remain approximately constant during the hydrolysis. This means that as long as ethoxide ions do not participate in the decomposition process, third order kinetics according to the mechanism in scheme 1 should be expected, in agreement with observation. The unreactivity of ethoxide ions towards methyl phenyl phosphonium compounds was proved by a study of the process
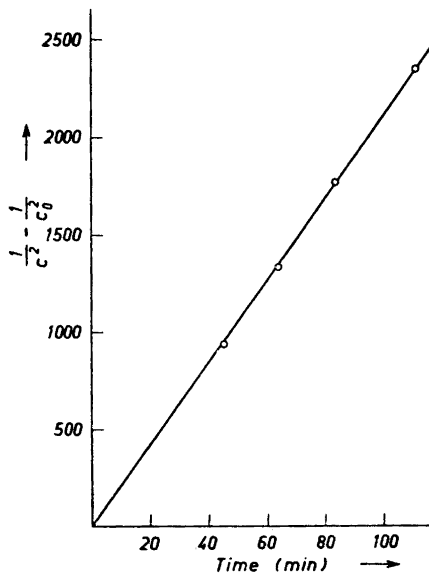
Fig. 1. Third order plot for the alkaline decomposition of equimolecular amounts of triphenyl methyl phosphonium bromide and sodium hydroxide (0.0479 M) in 74.8 % alcohol-water mixture at 60°C.
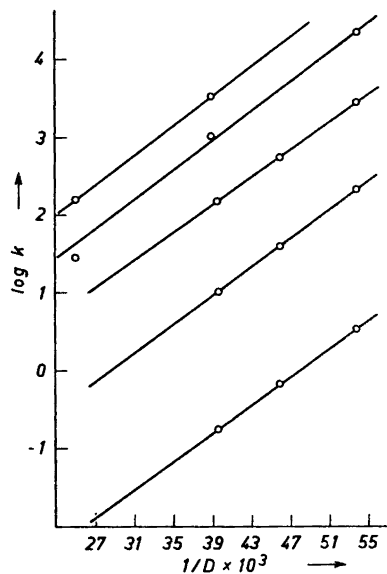
Fig. 2. Plot of log $k_{80°C}$ against $1/D$ of the solvent at 80°C for the alkaline decomposition of phosphonium bromides in alcohol-water mixtures. a) trimethyl phenyl, b) dimethyl diphenyl, c) methyl triphenyl, d) tetraphenyl and e) methoxymethylene triphenyl phosphonium bromides.

in ethoxide solution made from carefully dried alcohol and sodium. The result is shown in Fig. 3. The first minutes after the mixing of the reagents are characterized by a fast decomposition of the phosphonium compounds, whereafter the rate of decomposition rapidly decreases. The reaction stops when only 10—20 % of the phosphonium compound has reacted. The initial decomposition must therefore be due to traces of water in the ethoxide solution. From
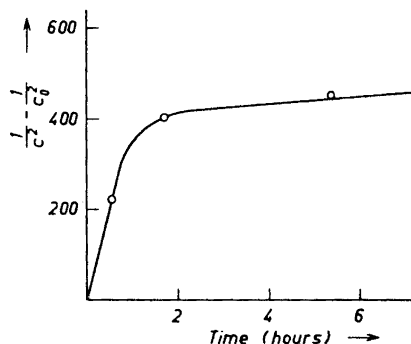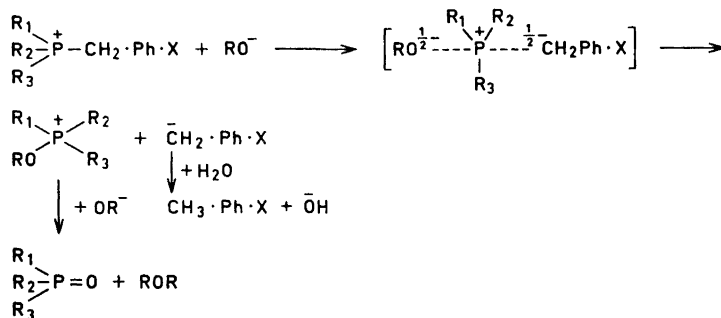

Fig. 3. Third order plot of the alkaline decomposition of dimethyl diphenyl phosphonium bromide in absolute alcoholic solution at 80°C.

the amount of phosphonium compound decomposed the water content in the ethoxide solution is estimated to 0.01 to 0.02 % by volume.

When the phosphonium salt contains a benzyl or p-substituted benzyl group, which is able to form an electronically more stabilized anion than the phenyl group, decomposition of the phosphonium compound in ethoxide solution is observed. In these cases the leaving group (benzyl or p-substituted benzyl groups) must be assumed to be sufficiently activated to be directly displaced by the ethoxide ion (S_N2 reaction):

$$
\begin{array}{l}
R_1 \\
R_2 \!-\! \overset{+}{P} \!-\! CH_2 \cdot Ph \cdot X \;+\; RO^- \longrightarrow \left[RO^{\tfrac{1}{2}-} \cdots \overset{R_1 \;\; R_2}{\underset{R_3}{\overset{+}{P}}} \cdots {}^{\tfrac{1}{2}-} CH_2 Ph \cdot X \right] \longrightarrow \\
R_3
\end{array}
$$

$$
\begin{array}{l}
R_1 \;\;+\;\; R_2 \\
\quad \overset{>}{P} \qquad +\; \bar{C}H_2 \cdot Ph \cdot X \\
RO \;\;\; R_3 \qquad \big\downarrow +H_2O \\
\quad \big\downarrow + OR^- \quad CH_3 \cdot Ph \cdot X \;+\; \bar{O}H \\
\\
R_1 \\
R_2 \!-\! P = O \;+\; ROR \\
R_3
\end{array}
$$

Scheme 2.

This scheme should give second order kinetics for the formation of toluene or p-substituted toluene, and offers a plausible explanation of the previous reported second order kinetics of the alkaline decomposition of triphenyl p-nitrobenzyl phosphonium chloride in 50 % alcohol-water mixture [1]. Parisek et al.[2] observed that toluene is formed much more rapidly than butyl ether during the decomposition of benzyl substituted phosphonium compounds in butoxide solution; thus, after 48 h 98 % toluene was formed as compared to only 8 % butyl ether. This result is also in agreement with a direct displacement of the benzyl group by the butoxide ion in the first step, followed by a slow decomposition of the intermediately formed phosphonium compound producing butyl ether and phosphine oxide.

Since triphenyl benzyl phosphonium chloride in ethoxide solution containing small amount of water was found to obey third order kinetics,[1] it is reasonable to assume that direct displacement of the benzyl group by OR^- or OH^- through attack at the phosphorus atom proceeds at a much slower rate than the reaction according to scheme 1 where a pentacovalent intermediate is formed. Only when the benzyl group contains strongly activating p-substituents as for example the nitro group, direct displacement (S_N2) appears to be the dominating mechanism.

THE EFFECT OF SUBSTITUENTS UPON THE ALKALINE DECOMPOSITION OF PHOSPHONIUM COMPOUNDS

In Table 1 are recorded the activation energies and the Arrhenius' frequency factors for the alkaline decomposition of different phosphonium compounds in various water-alcohol mixtures. The effect of the methyl group linked to

phosphorus is to increase the activation energy. This effect can be attributed to a decreasing availability of the d-orbitals of phosphorus for bonding during formation of the pentacovalent intermediate, in passing from tetraphenyl to trimethyl phenyl phosphonium compounds, in accordance with the view of Craig et al.[8] that substituents with $+ I$ effect make the d-orbitals of phosphorus more diffuse and therefore less suitable for bonding. The frequency factors of the alkaline decomposition of phosphonium compounds are remarkable high, and cause the decompositions to proceed with measureable rates in spite of unfavourable activation energies. The differences between the frequency factors for the decomposition of the different compounds are small, showing that steric hindrance plays a minor role.

An idea about the ion distance when the phosphonium and hydroxyl ions are reacting is obtained from the expression predicted for the medium effect [9]:

$$\ln \, k = \ln \, k_0{}' - \frac{N \cdot Z_A \cdot Z_B \cdot e^2}{D \cdot RT \cdot r^*}$$

where k = calculated rate constant at the absolute temperature T, $k_0{}'$ = rate constant in a medium of infinite dielectric constant D, Z_A and Z_B are the charges of the reacting ions, e = electron charge, N = Avogadros number, R = gas constant and r^* is the average distance of the ions during reaction. Since the plots of log k against $1/D$ for the various methyl phenyl substituted phosphonium salts at 80°C give a series of straight and parallell lines (Fig. 2), it follows from the above expression that the r^*-values for the different phosphonium compounds are identical. The calculated value is found to be 2.3 Å. Due to the uncertainty of the dielectric constant of the medium between the colliding ions when these are approaching each other to within their van der Waals radii, all that can be said is that the r^*-value is of correct order of magnitude. However, the fact that the r^*-value is the same independent of substituents linked to phosphorus, supports the assumption that steric hindrance play a minor role in the reaction.

In the alkaline hydrolysis of phosphoryl compounds it was observed that conjugative substituents as for example alkoxy groups were able to increase the activation entropy for the nucleophilic displacement on phosphorus [10,11]. However, phenyl substituents linked to phosphorus did not show this effect, and it was accordingly concluded that the electronic effect of phenyl groups

Table 2. Infrared stretching frequencies of the methyl groups in methyl phenyl phosphonium bromides and stretching frequencies of the P=O group of corresponding phosphine oxides.

CH$_3$-bands in phosphonium bromides (cm^{-1})			P=O band in phosphine oxides (cm^{-1})			
$\overset{+}{(Me)_3P.Ph}$	$\overset{+}{(Me)_2P(Ph)_2}$	$\overset{+}{MeP(Ph)_3}$	$(Me)_3P=O$	$(Me)_2(Ph)P=O$	$Me(Ph)_2P=O$	$(Ph)_3P=O$
2962, 2888 (2945)	2935, 2880	2917, 2872	1150	1174	1192	1206

linked to phosphorus was mainly inductive [12] ($-I$). The same result was also obtained from studies of the UV spectra of phenyl phosphonic acids [13]. The approximate constancy of the frequency factors for the alkaline decomposition of methyl phenyl phosphonium salts (Table 1) is thus in agreement with observation in the phosphoryl series.

The infrared spectra of the phosphonium compounds, together with the spectra of the phosphine oxides formed during the alkaline decomposition, give information about the electronic effects of the substituent linked to phosphorus. In Table 2 are recorded the stretching vibration frequencies of the methyl group in the phosphonium compounds and of the phosphoryl groups of the corresponding phosphine oxides. The increasing positive charge on phosphorus upon introduction of phenyl substituents ($-I$ effect) will make the diffuse d-orbital more available for bonding [8]. This will result in a greater hyperconjugation effect on the C$-$H bonds of the methyl groups, and the C$-$H stretching frequency should decrease, in agreement with the data in Table 2. In the corresponding phosphine oxides the pd-orbital overlap between oxygen and phosphorus will increase, which correspondingly should increase the stretching frequency of the phosphoryl group. However, if the phenyl group was able to conjugate with the P$=$O group this effect would be expected to more than outweigh the inductive effect, as is the case for carbonyl compounds where the stretching frequencies of the carbonyl bands of acetone, acetophenone and benzophenone are found at 1709, 1685, and 1659 cm^{-1} respectively in chloroform solution [14]. The data in Table 2 show that the influence of the phenyl groups on the position of the phosphoryl bands in the phosphoryl series is exactly opposite to the carbonyl series. This supports the earlier conclusion that in organic phosphorus compounds with phenyl linked directly to phosphorus, the inductive effect of phenyl groups ($-I$) predominates.

REFERENCES

1. Aksnes, G. and Songstad, J. *Acta Chem. Scand.* **16** (1962) 1426.
2. Parisek, C. B., McEwen, W. E. and Vander Werf, C. A. *J. Am. Chem. Soc.* **82** (1960) 5504.
3. Grayson, M. and Keough, P. T. *J. Am. Chem. Soc.* **82** (1960) 3919.
4. Michaelis, A. *Ann.* **181** (1876) 359.
5. Meisenheimer, J., Casper, J., Höring, M., Lichtenstadt, L. and Samuel, W. *Ann.* **449** (1926) 213.
6. Fenton, G. W. and Ingold, C. K. *J. Chem. Soc.* **1929** 2350.
7. Michaelis, A. and Gleichmann, L. *Ber.* **15** (1882) 803.
8. Craig, D. P., Maccoll, A., Nyholm, R. S., Orgel, L. E. and Sutton, L. E. *J. Chem. Soc.* **1954** 332.
9. Scatchard, G. *Chem. Rev.* **10** (1932) 129.
10. Aksnes, G. *Acta Chem. Scand.* **14** (1960) 1515.
11. Ginjaar, L. *The Reactivity of Some Organophosphorus Compounds in Nucleophilic Substitution Reactions*, Thesis, Leiden 1960.
12. Hudson, R. P. and Keay, L. *J. Chem. Soc.* **1960** 1859.
13. Jaffe, H. H. *J. Chem. Phys.* **22** (1954) 1430.
14. Barrow, G. M. *J. Chem. Phys.* **21** (1953) 2008.