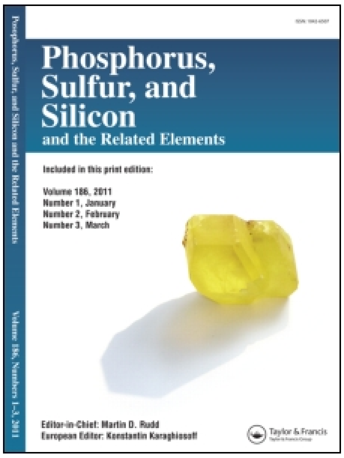


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SALT, SOLVENT AND SUBSTITUENT EFFECTS IN THE HYDROXIDE AND ALKOXIDE PROMOTED DECOMPOSITION OF PHOSPHONIUM COMPOUNDS

Gunnar Aksnes[a]
[a] Department of Chemistry, University of Bergen, Bergen, Norway

To cite this Article Aksnes, Gunnar(1977) 'SALT, SOLVENT AND SUBSTITUENT EFFECTS IN THE HYDROXIDE AND ALKOXIDE PROMOTED DECOMPOSITION OF PHOSPHONIUM COMPOUNDS', Phosphorus, Sulfur, and Silicon and the Related Elements, 3: 2, 227 — 238

To link to this Article: DOI: 10.1080/03086647708077717

URL: http://dx.doi.org/10.1080/03086647708077717

Phosphorus and Sulfur
1977, Vol. 3, pp. 227–238

SALT, SOLVENT AND SUBSTITUENT EFFECTS IN THE HYDROXIDE AND ALKOXIDE PROMOTED DECOMPOSITION OF PHOSPHONIUM COMPOUNDS †

GUNNAR AKSNES

Department of Chemistry, University of Bergen, 5014 Bergen, Norway

After studies by Ingold and coworkers[1,2] on the alkaline decomposition of phosphonium salts in the late twenties and early thirties, a period of nearly thirty years passed before a renewal of the field took place. During the last fifteen years, the kinetics of the alkaline decomposition of phosphonium salts has usually been discussed according to the following mechanistic scheme:[3-7]

$$\overset{+}{R_4P} + HO^- \underset{-1}{\overset{1}{\rightleftarrows}} R_4P{-}OH \underset{-2}{\overset{2\,HO^-}{\rightleftarrows}}$$

$$\begin{tikzcd} R_4PO^- \arrow[r, "\text{(3) rate}", "\text{determ.}"'] & R_3P{=}O + R^- \arrow[d, "H_2O"] \\ & RH + HO^- \end{tikzcd}$$

Reaction Scheme A

According to Scheme A the kinetic order is first order in the concentration of phosphonium cations and second order in the concentration of hydroxyl ions. A very good leaving group such as *p*-nitrobenzyl follows first order with respect to hydroxyl ions.[6] This can be explained if the decomposition of the pentacovalent stage is no longer rate determining.

Less systematic work has been done on the salt effect in the alkaline decomposition of phosphonium compounds.[7] To avoid a disturbing salt effect, it is often usual to add neutral salt in order to keep the ionic, strength approximately constant during the run. Inspection of the proposed reaction Scheme A shows that a considerable kinetic salt effect ought to be observed if no neutral salt is added since the reaction takes place between oppositely charged ions.

Introducing the Debye-Huckel expression for the activation coefficients in the Bronsted equation,

$$k = k_0 \frac{\gamma_A \cdot \gamma_A}{\gamma_\ddagger} ,$$

gives, as a first approximation:[8]

$$\ln k = \ln k_0 + 2Z_A \cdot Z_B\, \alpha \cdot \sqrt{I} \qquad \text{(I)}$$

Since the two ions, the phosphonium cation and the hydroxyl ion, are of opposite charges, a strong rate decrease is expected with increasing initial concentration of reactants. If no neutral salt is added, there ought also to be a rate increase during the kinetic run since the ionic strength is steadily decreasing. Experimental data are at first glance very confusing. Some representative data are collected in Figure 1:

a) Addition of neutral salt gives the expected rate decrease.
b) Increasing the initial concentration of reactants shows a rate increase in spite of the fact that an increasing ionic strength ought to give the opposite effect.
c) Varying only the hydroxyl concentration gives a rate minimum around 0.5 M.

Regarding the kinetic salt effect, the rate expression in equation (I) can only be used at infinite concentration.

In a work on the alkaline decomposition of positively charged ammonium esters[9] (Figure 1 (d)), which

---

† Plenary Lecture. The Vth International Conference of Organic Phosphorus Chemistry, Gdansk, Poland, September 1974.

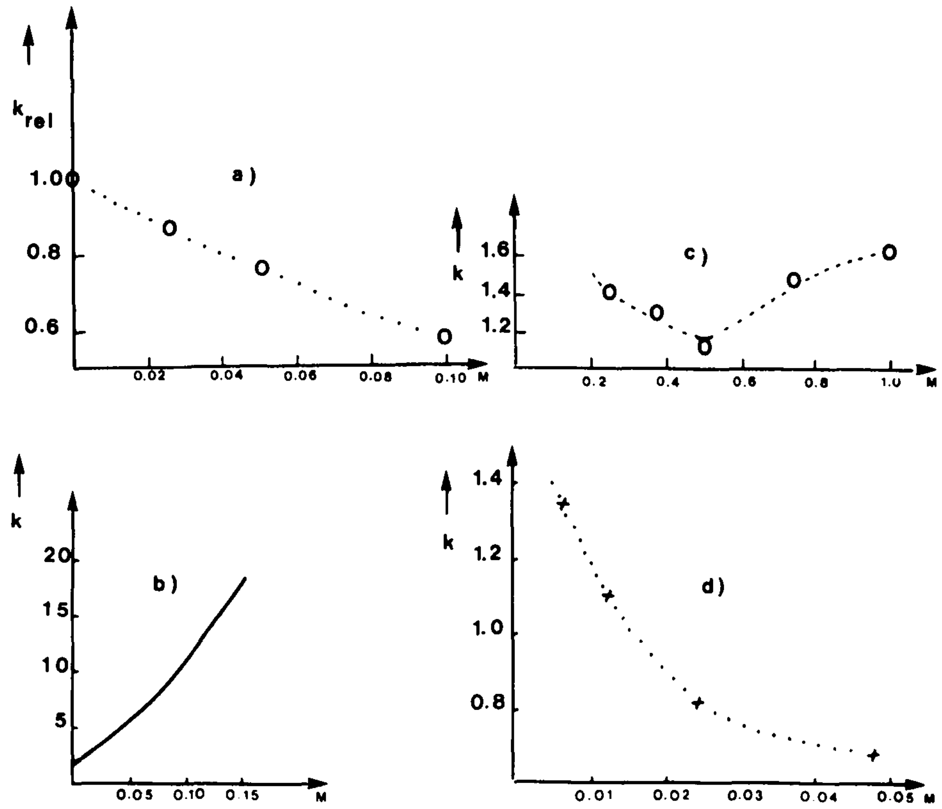


FIGURE 1 Salt effect in the alkaline hydrolysis of phosphonium salts. (a) Triphenylbenzyl bromide: 0.05 M, NaOH: 0.05 M with varying concentration of NaBr. (b) Varying initial concentrations of triphenylbenzyl bromide and NaOH (equimolar concentrations of reagents). (c) Tributyl-*p*-nitrobenzyl phosphonium bromide, 2.10^{-4} M varying concentrations of NaOH. (d) Varying initial concentrations of trimethyl ethoxybenzoyl ammonium bromide and NaOH (equimolar concentrations of reagents).

is somewhat similar to the present reaction, we used the following rate equation:

$$\log k = \log k^0 + \frac{2 Z_A \cdot Z_B \cdot A \cdot I^{1/2}}{1 + I^{1/2}} + BI \qquad \text{(II)}$$

where I is the ionic strength and B a constant taking care of the specific salt effect.

TABLE I
Specific salt effect (β-values)

Reactants		β-value
$Me_3\overset{+}{N}(CH_2)_3COOMe$	HO^-	0.1
$Ph_3\overset{+}{P}CH_2PH$	HO^-	10

The data in Table I, where the alkaline hydrolysis of ammonium ester and benzyltriphenyl phosphonium chloride have been compared, reveal a very strong specific salt effect in the alkaline decomposition of phosphonium salts. The positive rate effect which was first observed by Hoffmann,[7] is due primarily to the phosphonium cation. The phosphine oxide produced also has an accelerating effect,[7] but much smaller. The specific salt effect is not limited to phosphonium salts since corresponding ammonium salts also give the same effect.[7] Further, onium salts containing aromatic substituents have much stronger specific salt effects than those with aliphatic substituents (Figure 2).

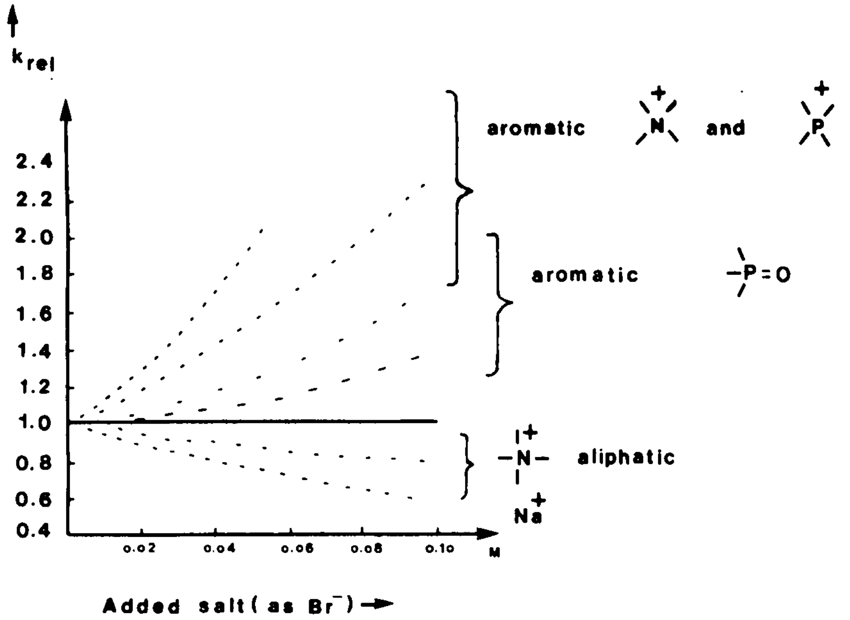
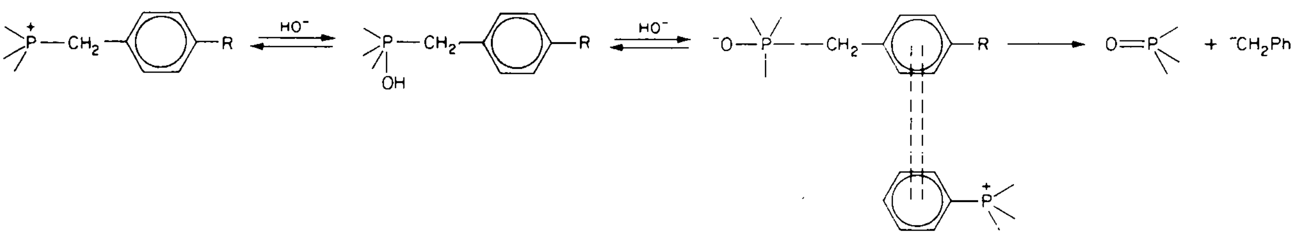


FIGURE 2 The influence of different salts and phosphine oxides on the rate of decomposition of aromatic phosphonium salts.

In our opinion, since the specific salt effect is primarily caused by aromatic onium cations, a charge-transfer complex between the rate determining transition state and the aromatic group of the onium cation seems likely:



Evidence for a charge-transfer complex is also seen from the data of Hoffmann[7] where the alkaline decomposition of differently *p*-substituted benzyl phosphonium salts is reported. It is found that electron accepting substituents strongly accelerate the specific salt effect in accordance with an expected increase in strength of the charge transfer complex with increasing negative charge on the leaving group.

The discussion so far shows that one has to distinguish between two different salt effects in the alkaline decomposition of phosphonium compounds: (i) kinetic salt effect; and (ii) specific salt effect of the phosphonium cations. Since the two salt effects work in opposite directions, the rate increase during the reaction due to the kinetic salt effect (decrease of the ionic strength of the reaction solution) is counteracted by a simultaneous rate decrease due to the decrease of the concentration of phosphonium cation (Figure 3). This explains the very nice fit to a third order rate equation often obtained in the phosphonium salt decomposition, which obeys the third order rate law often to more than 90% completion. The two salt effects are accordingly of comparable magnitude, but individual variations are expected depending upon the substituents linked to phosphorus. The alkaline decomposition of phenyltrimethylphosphonium bromide is especially noteworthy due to its strong positive deviation from the rate law (Figure 4). With only one phenyl substituent linked to phosphorus, the specific salt effect is much smaller than the kinetic salt effect resulting in an increase of the third order rate constant with time.

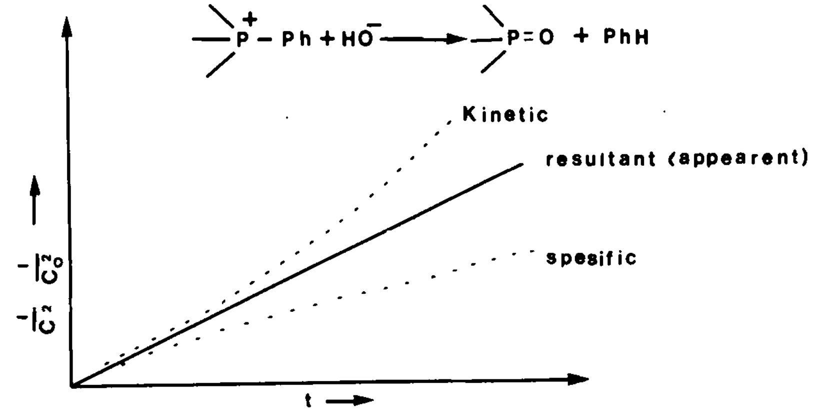


FIGURE 3 The influence of kinetic and specific salt effects on the alkaline decomposition of aromatic phosphonium salts.

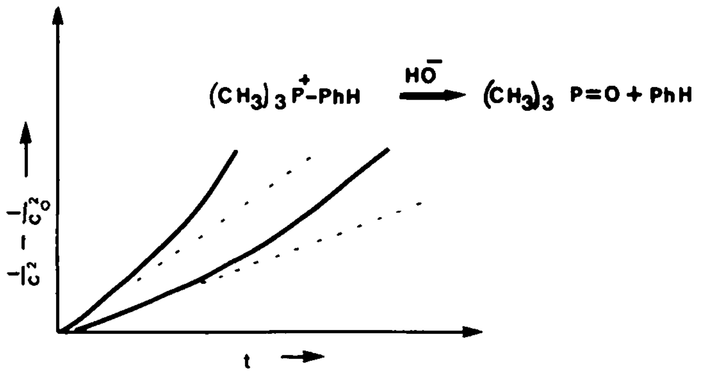


FIGURE 4 Third order rate plot for the alkaline decomposition of trimethyl phenyl phosphonium bromide at 75° and 80°C in 75% ethanol-water.

SOLVENT EFFECT

It has been recognized for a long time that the alkaline decompositions of phosphonium salts are strongly accelerated by organic solvents. At our institute, we have made a systematic study of solvent effects on the alkaline decomposition of tetraphenylphosphonium chloride.[10] Some of our data are shown in Table II. We recognize, first of all, the great difference in effect in hydroxylic and non-hydroxylic organic solvents. The rate increase from H_2O to 80% EtOH-H_2O is 600, to 80% dioxane-H_2O 1.6×10^8, and to 70% DMSO-H_2O 3.4×10^9.

TABLE II

Alkaline decomposition of $Ph_4\overset{+}{P}$ in various H_2O-organic solvent mixtures

Volume % organic solvent	EtOH–H_2O k_{50} $l^2M^{-2}min^{-1}$	EtOH–H_2O E kcal/M	EtOH–H_2O ΔS* e.u.	Dioxane-H_2O k_{25} $l^2M^{-2}min^{-1}$	Dioxane-H_2O E kcal/M	Dioxane-H_2O ΔS* e.u.	DMSO–H_2O k_{25} $l^2M^{-2}min^{-1}$	DMSO–H_2O E kcal/M	DMSO–H_2O ΔS* e.u.
0	0.04	33.5	+ 31	5.3×10^{-4}	33	+ 29	5.3×10^{-4}	33	+ 29
10				2.3×10^{-3}	32	+ 28	1.5×10^{-3}	32	+ 26
20	0.085			7.1×10^{-3}	31	+ 25	5.8×10^{-3}	30	+ 22
30				2.8×10^{-3}	30	+ 24	4.9×10^{-2}	29	+ 18
40				2.0×10^{-1}	28	+ 23	5.8×10^{-1}	25	+ 13
50	0.695			3.5	21	+ 5.4	3.9×10	24	+ 18
60				5.6×10	18	−1.5	1.6×10^{4}	22	+ 27
70				2.0×10^{3}	15	−1.8	1.8×10^{6}	17	+ 16
80	24.4	29	+ 29	8.9×10^{4}	11	−10			

Since dioxane and the dipolar solvent DMSO have such outstanding solvent effects, it is immediately clear that the difference in solvation of hydroxyl ions in hydroxylic and aprotic media is the dominating solvent effect which influences the rate. The activation energy differences in water and water-organic solvents show a tremendous decrease in water-apolar solvent mixtures amounting to 17-18 kcal/mole from water to 70% water-aprotic solvent. That this is mainly a solvation effect is shown by the corresponding decrease in entropy, which means that there is less disordering of solvent molecules from reactants to transition state in the organic solvent mixture in agreement with the lower solvation of the ions.

It is interesting to analyze the data according to the Born-Scatchard electrostatic model for the solvent effect:

$$\ln k = \ln k_0 - \frac{N \cdot Z_A \cdot Z_B e^2}{DRTr^*}$$

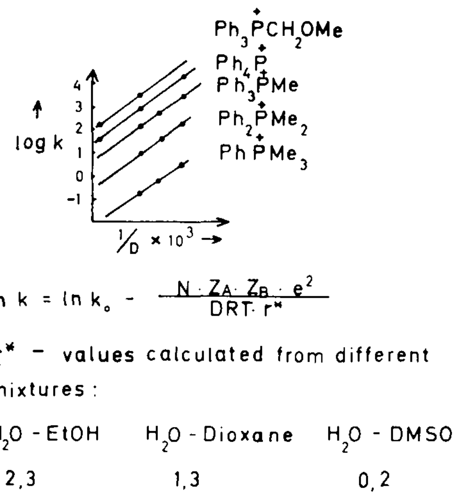


FIGURE 5 The dependence of dielectric constant in ethanol-water mixtures on the rate of alkaline decomposition. Calculated collision radius of activated complexes in different H_2O-organic solvent mixtures.

In Figure 5 some representative data are plotted for the alkaline phosphonium ion decomposition in ethanol-water. The straight line dependence is rather good, but the value for the closest approach of the reacting ions, 2.3 Å, is much too low. Results in aprotic solvent, and especially in DMSO where the calculated r* value is 0.2 Å, reveals that the model is devoid of any physical meaning. This is, of course, due to the neglect of short range solvation forces in the model. A better understanding of the solvent effect is obtained by comparing the rate with the basicity function H_- (Table III).

TABLE III

Volume % organic solvent	$EtOH-H_2O$		$DMSO-H_2O$	
	log k_{50}	$H-$	log k_{25}	H_-
0	−1.37	11.74	−3.28	11.74
10			−2.85	12.94
20	−1.07	12.40	−2.24	14.28
30			−1.31	15.40
40			−0.24	16.41
50	−0.16	13.06	+1.59	17.23
60			+4.19	17.93
70			+6.25	18.87
80	1.39	13.6		

In Figure 6, the rates in ethanol and DMSO water mixtures are plotted against H_-. It is seen that the rate at the beginning increases more rapidly the proportionality to H_-. This may indicate not only that the reacting ions are changing their solvation but also that the transition state is changing. The latter is better solvated in organic solvent than in water, thus lowering its activation energy (Figure 7).

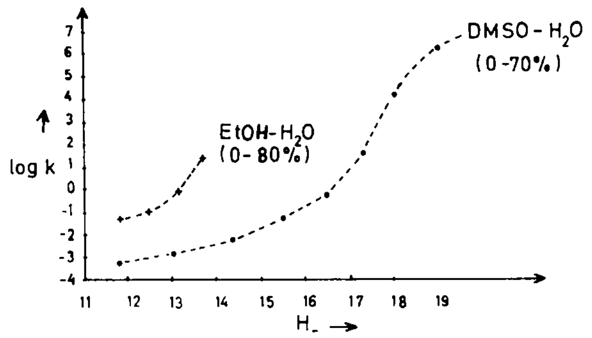


FIGURE 6 The function between rate and the acidity function H_-.

ISOTOPE EFFECT

Thus far salt, as well as solvent, effects afford evidence in favor of the postulated mechanism for the phosphonium ion decomposition. We have also done some measurements in D_2O-organic solvent mixtures. If the proton

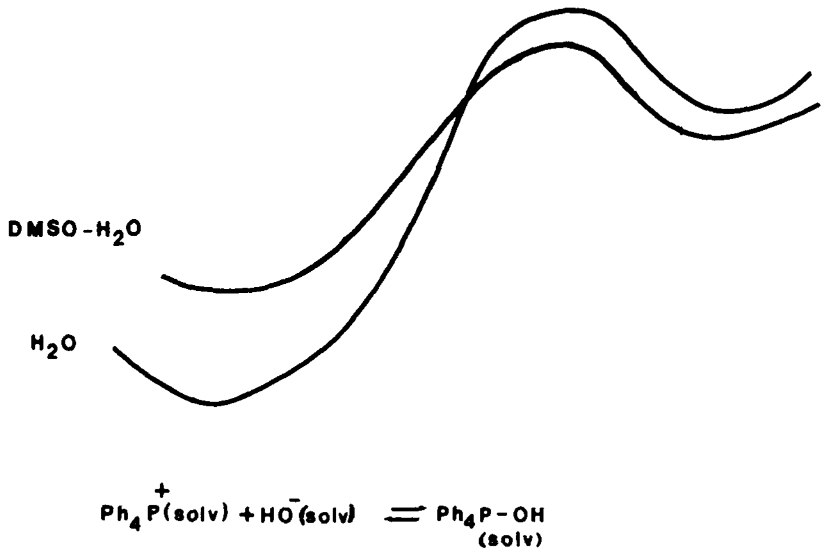


FIGURE 7 Solvation scheme in the decomposition of $Ph_4P^+OH^-$ in H_2O and H_2O–DMSO.

is entirely lost from the phosphorus atom before the transition state, only a secondary isotope effect is expected. If, however, proton removal and splitting of the P–C bond is synchronous, a primary isotope effect is expected which will result in a rate decrease in D_2O.

The rate in D_2O is around twice that in H_2O thus ruling out the synchronous mechanism. The magnitude of the secondary isotope effect is of the order expected from the difference in basicity of HO^- and DO^-.[12,13]

SUBSTITUENT EFFECT

A great deal of work has been done in elucidating the substituent effect in the alkaline phosphonium ion decomposition.[1-4] Ingold[1,2] noted that the rate of decomposition increases with increasing stability of the leaving group. This has later been verified by many workers.[14] The rates of substituted aromatic leaving groups are found to correlate with the Hammet constant. The influence of the non-leaving group on phosphorus on the rate is also well documented; it causes an increase with increasing electronegativity.[6]

A much-celebrated field in recent years has been the study of substituent effects of cyclic phosphonium compounds, especially 4- and 5-membered ring systems, the so-called phosphetanes and phospholane derivatives.[14]

In this paper my discussion is limited to investigations of hydroxyalkyl-substituted phosphonium compounds. In 1963, Grayson,[15] published a thorough study of the kinetics of the alkaline decomposition of α-hydroxy substituted phosphonium salts showing that the mechanism was different in low and high hydroxyl concentrations. The decomposition of β-hydroxy substituted phosphonium compounds is even more complicated as the number of isolated products shows (Figure 8). Strong evidence for formation of a vinyl phosphonium intermediate has been brought forward in recent years.[16] I will report here some kinetic studies which further support this view and show under which solvent condition the latter reaction mechanism predominates.

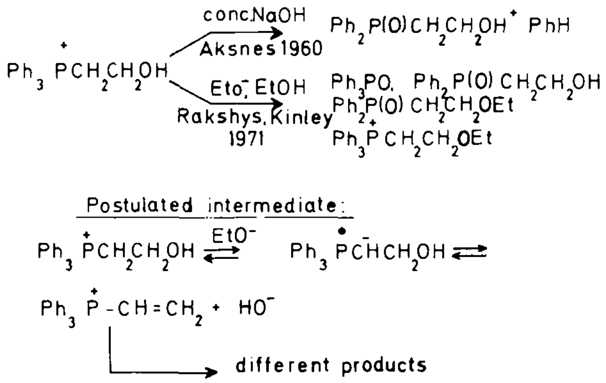
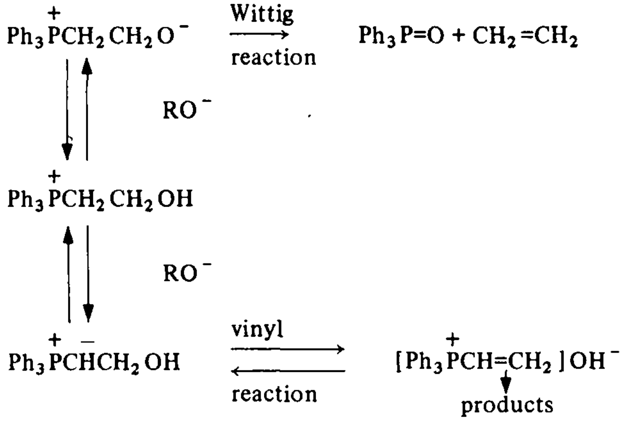


FIGURE 8 Reaction products for alkaline decomposition of $Ph_3\overset{+}{P}CH_2CH_2OH$, and postulated intermediates.

TABLE IV
Alkaline hydrolysis (HO^- and EtO^-) of:

Phosphonium salt	Solvent % EtOH	Rate $l^2M^{-2}min^{-1}$
$Ph_3\overset{+}{P}CH_2CH_2OH$	74	3.9
	84	10.5
	94	30.5
	100	5.4
$Ph_3\overset{+}{P}CH_3$	74	2.4
	84	9.4
	94	46.4
	100	0.01

A comparison of the hydrolysis of β-hydroxyethyl- and methyl phosphonium compounds shows that the decomposition rates in alcohol/water mixture is comparable whereas the rate in absolute alcohol is several hundred times higher (Table IV). The mechanism must accordingly be different in absolute alcohol. Two mechanisms can be postulated:



The Wittig type reaction can be ruled out since the reaction is overall third order, first order in phosphonium cation and second order in alkoxide. If the vinyl phosphonium intermediate takes part in the reaction, three different phosphonium salts will be present in the reaction solution in alcohol: β-hydroxyethyl, vinyl- and β-ethoxyethyl phosphonium salts. Kinetic and product studies of these three salts have been carried out (Table V). The high concentration of β-ethoxyethylphosphine oxide in the decomposition of the β-hydroxyethyl salt, both in absolute alcohol and in 74% alcohol, shows that the vinyl phosphonium salt must be an important intermediate in 74% ethanol also. The extremely slow reaction of pure vinyl phosphonium salt and β-ethoxyethylphosphonium salt in absolute alcohol is due to the absence of hydroxyl ions. The comparable rate of the three salts in water containing alcohols indicates that a rapid equilibrium is established between the different species.

TABLE V
Rate and product analysis

% EtOH	$\overset{+}{Ph_3P}$–R	Ph₂P(O)–R $-CH_2CH_2OH$	$-CH_2CH_2OEt$	$-Ph$	Rate $l^2M^{-2}min^{-1}$
100	$-CH_2CH_2OH$	3	84	13	5.4
	$-CH{=}CH_3$	–	+	+	(0.03)
	$-CH_2CH_2OEt$	–	+	+	(0.03)
100 + 1 eqv. H_2O	$-CH_2CH_2OH$	5	84	11	13.5
	$-CH{=}CH_2$	0	88	12	7.1
	$-CH_2CH_2OEt$	0	83	17	7.1
74 +26 H_2O	$-CH_2CH_2OH$	16	63	21	4.6
	$-CH{=}CH_2$	12	66	22	4.1
	$-CH_2CH_2OEt$	16	65	19	5.0

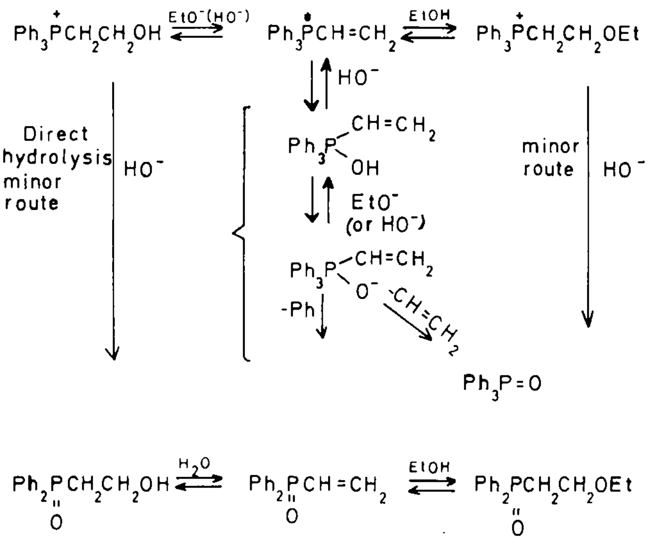


FIGURE 9 Mechanistic scheme for alkaline decomposition of $\overset{+}{PH_3P}CH_2CH_2OH$.

The results of our kinetic studies are summarized in the reaction scheme in Figure 9. The ease of vinyl phosphonium formation is also confirmed by Kunz in a publication in a recent issue of this journal.[17]

ALKOXIDE DECOMPOSITION

It was stated earlier that phosphonium compounds containing no β-hydroxyl group, such as vinyl- and ethoxyethyltriphenylphosphonium salts, also decompose in absolute ethanolic solution. However, this reaction, after an initial rapid phase, was extremely slow (Figure 10). We believe that the initial reaction is due to a very small amount of water (less than 0.01%) which is difficult to get rid of. Investigation of the slow reaction for propyltriphenylphosphonium iodide gives a reasonable fit to a third order rate law.

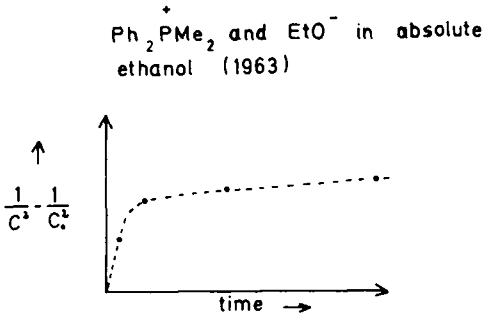


FIGURE 10 Reaction of $Ph_2\overset{+}{P}Me_2$ and EtO^- in absolute ethanol.

However, if the alkoxide-promoted decomposition can proceed intramolecularly through a 5-membered phospholane ring structure, the decomposition is 10^3-10^4 times more rapid. We assume that the reaction in absolute ethanol proceeds though a hexacovalent intermediate,[18] and that the reason for the high rate of the 3-hydroxypropyl-substituted compound is due to the higher stability of a hexacovalent intermediate with phospholane structure (Figure 11).

The decomposition rate of *bis*(2-hydroxypropyl)diphenylphosphonium chloride is also high. In this case a diphospholane intermediate can be formed which ought to have an even more favorable entropy of activation (Figure 12). But since these compounds have two alkyl groups substituted on phosphorus instead of one in the mono compound, this ought to result in a less favorable activation enthalpy. The activation data in Table VI show this to be the case. Since the 3-hydroxypropyl-substituted phosphonium salts so clearly pointed to a decomposition mechanism with a hexacovalent intermediate or transition state, we chose to investigate the decomposition of tetraphenylphosphonium chloride in hydroxide and methoxide solution.[19] We used 0.1 M concs. of both phosphonium salt and base, the former in 99% methanol + 1% H_2O, the latter in 100% methanol. Both reactions obeyed third order kinetics with comparable rate constants. The activation parameters differed widely however:

$$E_{HO^-} = 43\text{ kcal}; \quad \Delta S^*_{HO^-} = +63\text{ e.u.}$$

$$E_{MeO^-} = 32\text{ kcal}; \quad \Delta S^*_{MeO^-} = +21\text{ e.u.}$$

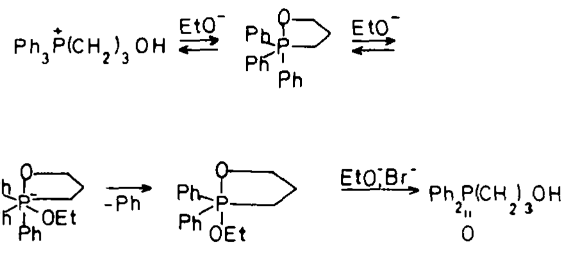


FIGURE 11 Reaction scheme for the alkaline decomposition of $Ph_3\overset{+}{P}(CH_2)_3OH$ in EtO^-/EtOH.

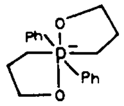


FIGURE 12 Postulated intermediate in the hydrolysis of $Ph_2\overset{+}{P}[(CH_2)_3OH]_2$.

TABLE VI

Compound	k_{RO^-} $l^2M^{-2}min^{-1}$	k_{HO^-} $l^2M^{-2}min^{-1}$	E kcal/M	ΔS* e.u.
$Ph_3\overset{+}{P}CH_2CH_2CH_2OH$	3.67[55]		29	+ 29
$Ph_2\overset{+}{P}(CH_2CH_2CH_2OH)_2$	0.14[75]		32	+ 40
$Ph_3\overset{+}{P}CH_2CH_2CH_3$	0.0036[60]			
$Ph_3\overset{+}{P}CH_3$		200	30.7	+ 34
$Ph_2\overset{+}{P}(CH_3)_2$		12	32.4	+ 33

It seems safe to conclude that such great differences in activation parameters can only be caused by different mechanisms. A lowering of activation energy is to be expected for splitting a phenyl group from a negatively charged hexacovalent complex as compared with a pentacovalent complex, but the greater restriction laid upon its formation will at the same time make the activation entropy less positive.

ACKNOWLEDGMENTS

I would like to express my sincere thanks for cooperation from my students, especially Miss Anna Eide, and further to my coworkers Doctor Fayez Khalil, University of Alexandria, Egypt, and Doctor Piotr Majewski, Technical University, Lodz, Poland.

REFERENCES

1. G. W. Fenton and C. K. Ingold, *J. Chem. Soc. (London)* 2342 (1929).
2. L. Hey and C. K. Ingold, *J. Chem. Soc. (London)* 531 (1933).
3. K. F. Kumli, W. E. McEwen, and C. A. Van der Werf, *J. Am. Chem. Soc.* 81, 3805 (1959).
4. W. E. McEwen, K. F. Kumli, A. Bladé-Font, M. Zanger, and C. A. Van der Werf, *J. Am. Chem. Soc.* 86, 2378 (1964).
5. G. Aksnes and J. Songstad, *Acta Chem. Scand.* 16, 1426 (1962).
6. G. Aksnes and L. J. Brudvik, *Acta. Chem. Scand.* 17, 1616 (1963); and 21, 745 (1967).
7. H. Hoffmann, *Justus Liebigs Ann. Chem.* 634, 1 (1960).
8. See for example: A. A. Frost and R. G. Pearson, *Kinetics and Mechanism* (John Wiley, 1961), p. 150.
9. G. Aksnes and J. E. Prue, *J. Chem. Soc.* 103 (1959).
10. Fayez Y. Khalil and G. Aksnes, *Acta Chem. Scand.* 27, 3832 (1973).
11. E. S. Amis, *Solvent Effects on Reaction Rates and Mechanism* (Academic Press, 1966).
12. K. Wiberg, *Chem. Rev.* 55, 713 (1955).
13. C. A. Bunton and V. J. Shiner, Jr., *J. Am. Chem. Soc.* 42, 3207 (1961).
14. For a review see for example R. Luckenbach, *Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related*

Elements (Georg Thiem Pub., Stuttgart, 1973).
15. M. Grayson, *J. Am. Chem. Soc.* **85**, 79 (1963).
16. J. W. Rakshys, Jr. and S. V. McKinley, *Chem. Commun.* 1337 (1971).
17. H. Kunz, *Phosphorus* 3, 273 (1974).
18. G. Aksnes and A. Eide, *Phosphorus* **4**, 209 (1974).
19. G. Aksnes, F. Y. Khalil, and P. J. Majewski, to be published.