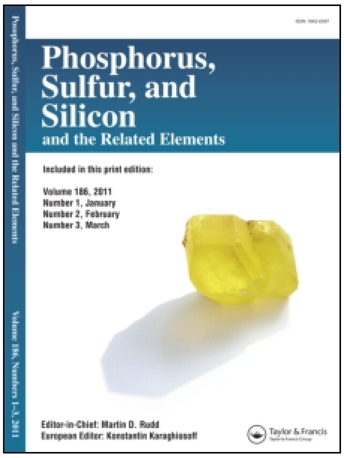

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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Gunnar Aksnes[a]; Fayez Y. Khalil[ab]; Piotr J. Majewski[ac]
[a] Department of Chemistry, University of Bergen, Bergen-Univ., Norway [b] Department of Chemistry, Faculty of Science, University of Alexandria, Alexandria, Egypt [c] Technical University, Lodz, Poland

To cite this Article Aksnes, Gunnar , Khalil, Fayez Y. and Majewski, Piotr J.(1977) 'KINETIC STUDY OF ALKOXIDE PROMOTED DECOMPOSITION OF ORGANIC PHOSPHONIUM COMPOUNDS Evidence for Hexacovalent Intermediate', Phosphorus, Sulfur, and Silicon and the Related Elements, 3: 2, 157 — 161

To link to this Article: DOI: 10.1080/03086647708077705

URL: http://dx.doi.org/10.1080/03086647708077705

Phosphorus and Sulfur
1977, Vol. 3, pp. 157–161

KINETIC STUDY OF ALKOXIDE PROMOTED DECOMPOSITION OF ORGANIC PHOSPHONIUM COMPOUNDS

Evidence for Hexacovalent Intermediate

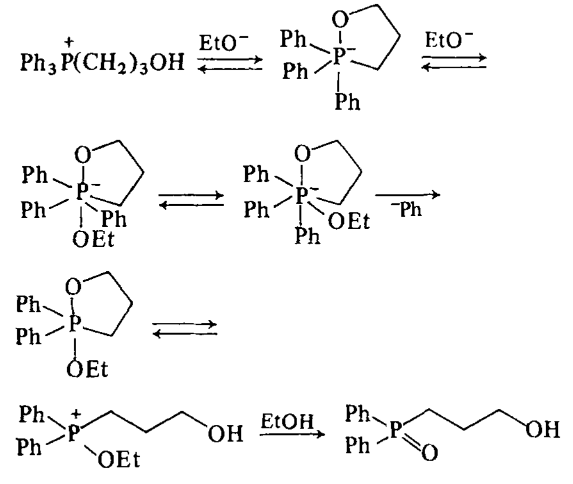
GUNNAR AKSNES, FAYEZ Y. KHALIL† and PIOTR J. MAJEWSKI‡

Department of Chemistry, University of Bergen 5014 Bergen-Univ., Norway

(*Received April 5, 1976*)

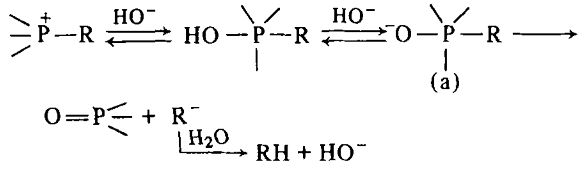
This study reports rate data of the alkoxide promoted decomposition of triphenyl 3-hydroxypropyl phosphonium chloride, diphenyl di(3-hydroxypropyl)phosphonium chloride, and tetraphenyl phosphonium bromide. Comparison of kinetics, rate constants, and activation parameters of the alkoxide promoted decompositions points to different mechanism as compared to the hydroxyl promoted reaction. The alkoxide reaction is believed to proceed via a hexacovalent intermediate. Reasons for the hexacovalent route are discussed.

In a communication from this institute some time ago evidences for a hexacovalent intermediate or transition state in the ethoxide promoted decomposition of triphenyl 3-hydroxypropyl phosphonium chloride were reported:[1]



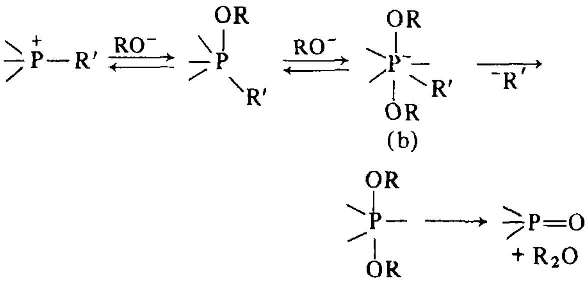
Scheme 1

In hydroxyl initiated decomposition of phosphonium compounds the intermediates in the reactions are not believed to pass beyond the pentacovalent state because the ionized phosphorane is assumed to be sufficiently energetic to expel the carbanion:



Scheme 2

However, when alkoxide ion is the attacking nucleophile the formation of the pentacovalent anion intermediate through splitting of the O—C bond in RO—P—R constitutes a higher energetic pathway than the cleavage of the O—H bond in H—O—P—R. Under such conditions attack of alkoxide on phosphorus forming a hexacovalent intermediate might well be the preferred pathway.



Scheme 3

When the rate determining step follows after the formation of the anion intermediates (a) or (b) in Scheme 2 and 3, the presence of a pentacovalent or a hexacovalent intermediate cannot be distinguished

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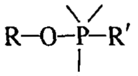
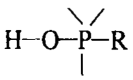
† Department of Chemistry, Faculty of Science, University of Alexandria, Alexandria, Egypt.

‡ Technical University, Lodz, Poland.

kinetically since both pathways will give the same reaction order, i.e. first order in phosphonium ions, and second order in HO^- or RO^-. But the ionization of the O—R bond by attack of RO^- on R in  $R{-}O{-}\underset{|}{\overset{\backslash\,/}{P}}{-}R'$ would be expected to have a higher activation energy because the pentacovalent state of phosphorus has little electron accepting ability on the ether oxygen.

Grayson and Keough[3] have reported that the *p*-nitrobenzyl group in phosphonium salts is easily displaced in alkoxide solution giving quantitatively *p*-nitrotoluene, phosphine oxide, and ether. The benzyl group could also be displaced under the same conditions, but the phenyl group in alkyl phenyl phosphonium compounds was reported to be unreactive. This is in accordance with our observations. However, we have found that the rate of displacement of phenyl increases strongly when alkyl groups are substituted by phenyl groups in the hydroxyl as well as alkoxide promoted decomposition.[4] The rate can also be accelerated by adding dipolar solvents.[10,20,21] Thus, tetraphenyl phosphonium bromide in acetone-rich media has a sufficiently high rate of decomposition in methoxide solution to be followed kinetically (Table (III).

The specially high rate of HO^- as well as RO^- promoted decomposition of *p*-nitrobenzyl substituted phosphonium salts needs some further comments. We have earlier shown that the alkaline decomposition of *p*-nitrobenzyl substituted phosphonium salts follows an overall second order kinetics, first order in phosphonium ions, and first order in hydroxyl ions.[4] The stabilized *p*-nitrobenzyl anion formed in this case might lower the activation energy sufficiently for direct displacement of the leaving group to occur without preceding ionization. If this is so, hydroxyl and alkoxide promoted decomposition ought to give comparable rates. But why should not ionization of  $H{-}O{-}\underset{|}{\overset{\backslash\,/}{P}}{-}R$ occur prior to displacement when proton abstractions are known to be rapid processes? A possible answer to this question might be found in the difference in ionization tendency of the P—O—H group in apical and equatorial positions. Due to the long and weak P—OH bond in apical position, the OH-group ought to show very little acidic properties, and hence will be much less acidic than the OH-group in equatorial position where π-bonding from oxygen to phosphorus can occur to some extent. Ramirez and Ugi have calculated that $(HO)_4PO^-$, with equatorial placement of O^-, is 28 kcal/M more stable than that with O^- in apical position.[6] But this means that pseudorotation is required before ionization can take place, and it might well be that the route: pseudorotation, followed by ionization of the OH-group, together has a higher energy requirement than the direct displacement of the *p*-nitrobenzyl group from the neutral phosphorane.

The unsubstituted benzyl group is more difficult to displace than the *p*-nitrobenzyl group in phosphonium salts. The hydroxyl promoted displacement of the former is 22 kcal/M as compared with 18 kcal/M for the latter.[7] The reaction obeys also fairly well second order dependence on HO^-. Extensive pseudorotation of the neutral phosphorane is, however, not expected in the hydroxyl reaction because the products from optically active phosphonium compounds show variable degrees of racemization, and often nearly complete inversion.[8] In the much slower alkoxide reaction, the neutral phosphorane ought to exist much longer, and the nearly complete racemization observed[9] in the product points to extensive pseudorotation of the phosphorane before displacement of the benzyl group.

When phenyl is the leaving group in the phosphonium salt the decomposition rate is always second order in base (HO^- or RO^-). The activation energy is also much higher than for benzyl as leaving group, between 30 and 40 kcal/M depending upon the other substituents linked to phosphorus.[4] It is reasonable to expect that an anion intermediate is required (pentacovalent or hexacovalent) in order to break the P—C bond and expel the phenyl group. We have earlier shown[10,20,21] that the isotope ratio, k_{DO^-}/k_{HO^-} in the hydroxyl promoted reaction is greater than one in the decomposition of tetraphenyl phosphonium chloride. This is a further strong evidence for the presence of a pentacovalent anion intermediate prior to displacement of the phenyl group.[20,21]

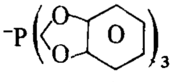
With regard to the probability of a hexacovalent intermediate in the alkoxide promoted decomposition of phenyl substituted phosphonium salts, it might be mentioned that compounds such as PF_6^- and  are well known.[11] Westheimer and co-workers have also detected the presence of $RP(OPh)_5^-$ in a mixture of $RP(OPh)_4$ and PhO^- in aprotic solvent.[12] Ramirez and co-workers have several times postulated similar intermediates.[13-15] The stability of hexacovalent phosphorus compounds seems to increase with increasing electronegativity of substituents, and is greatly stabilized when the substituents are part of five-membered phospholane rings.

TABLE I

Rates and activation parameters for the decomposition of propyl and 3-hydroxypropyl substituted phosphonium chlorides with sodium ethoxide in absolute ethanol. Equimolecular concentrations (0.07–0.1 M) of reactants were used

Compound	Rate constants, $k(l^2M^{-2}min^{-1})$ and reaction temperatures					*Activation parameters*	
						E kcal/M	log A
$Ph_3\overset{+}{P}CH_2CH_2CH_2OH$	$0.91^{45°}$	$1.87^{50°}$	$3.67^{55°}$	$7.3^{60°}$	(calc.)	29	20
$Ph_2\overset{+}{P}(CH_2CH_2CH_2OH)_2$	$0.016^{60°}$ (calc.)	$0.0344^{65°}$	$0.0703^{70°}$	$0.138^{75°}$		32	22
$Ph_3\overset{+}{P}CH_2CH_2CH_3$				$0.003^{60°}$			

RESULTS AND DISCUSSION

The rate of alkoxide promoted decomposition of alkyl phenyl substituted phosphonium salts is so slow that the compounds are less suited for kinetic studies. In Table I is, however, quoted the approximate value of the rate constant of the ethoxide promoted decomposition of *n*-propyl triphenyl phosphonium iodide in absolute ethanol at 60°C. Within the accuracy of the experimental procedure the rate was found to be dependent on the square of the ethoxide concentration. However, introduction of a hydroxyl group in 3-position of the propyl substituent is seen to have a dramatic rate increasing effect on the decomposition (Table I). On comparing the rates of hydroxyl promoted decomposition of similar substances (Table II), it is seen that the rate of the 3-hydroxypropyl substituted compound is very similar to the rate of the methyl substituted compound. This is also expected if the mechanism follows the pentacovalent anion route (Scheme 2). But a similar mechanism in the alkoxide decomposition could not explain the more than 2000 times rate increase from propyl to the 3-hydroxypropyl substituted compound. We conclude therefore that the mechanism of the alkoxide reaction differs from the hydroxyl reaction, and, in agreement with an earlier assumption,[1] postulate a hexacovalent route (Scheme 1). The rate increase in the 3-hydroxypropyl substituted compound as compared to the *n*-propyl substituted one is attributed to the favourable phospholane structure in the penta- and hexacovalent intermediates of the former, obtained by an intramolecular alkoxide attack. The rate increase is in fact of the same magnitude as the increase in rate of the hydroxyl promoted decomposition in going from dimethyl- to tetramethylene diphenyl phosphonium salts where the latter has also a similar advantage of a five-membered phospholane ring in the reaction intermediates.[5]

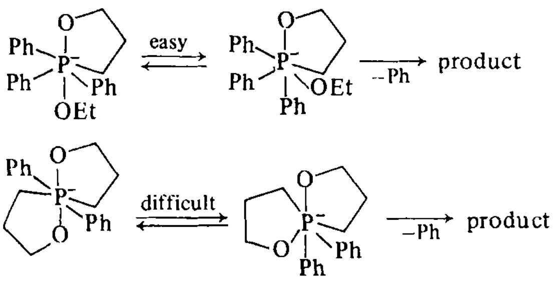
TABLE II

Rates of HO^--promoted decomposition of phosphonium salts in 74% $EtOH\text{-}H_2O$ at 50°C

Compound	$k(l^2M^{-2}min^{-1})$
$Ph_3\overset{+}{P}CH_3$	2.4
$Ph_3\overset{+}{P}CH_2CH_2OH$	3.9
$Ph_3\overset{+}{P}CH_2CH_2CH_2OH$	1.3

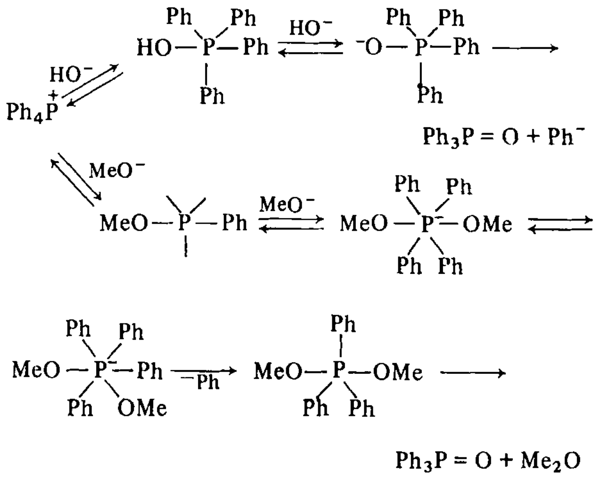
With regard to the phospholane effect we felt that a study of the alkoxide promoted decomposition of di(3-hydroxypropyl–diphenyl phosphonium salt might be quite interesting since a symmetrical hexacovalent intermediate with two phospholane rings might further stabilize the intermediates. The presence of two equivalent electronegative oxygen ether atoms in apical position should also heighten the stability. We were surprised to find that the rate of decomposition of this compound was much slower than the rate of the monosubstituted 3-hydroxypropyl compound (Table I). However, several reasons might give rise to the observed slower rate. We have earlier observed that the rate of decomposition of phosphonium salt decreases considerably with increasing alkyl substitution on phosphorus, being of the order 10 to 100 times slower per alkyl group.[4] This might explain part of the rate decrease, but a slower rate of decomposition of the hexacovalent intermediate might also be of importance. In order to split off one of the phenyl groups in the hexacovalent intermediates of the mono- and disubstituted 3-hydroxypropyl compounds one would expect that this is easiest obtained when the strongly electronegative alkoxy groups and the leaving phenyl group are in trans position to each other. Such a hexacovalent configuration would be expected to be more unstable than a structure with equivalent groups (oxygen or phenyl) in trans positions.

Pseudorotation would accordingly be required in order to reach the most reactive configuration:



But the rigid bicyclic compound might strongly resist pseudorotation in comparison with the monocyclic one.

As mentioned earlier in this paper we have observed that tetraphenyl phosphonium bromide is decomposed by methoxide ions at a rate sufficiently high to be followed kinetically in acetone-rich media. The rate of decomposition is considerably accelerated by adding dipolar solvent as acetone, dioxane, or dimethylsufoxide[10, 20, 21]. Table III summarizes data for the alkaline decomposition of tetraphenyl phosphonium bromide with HO^- as well as CH_3O^- in absolute methanol, 25% acetone-methanol, and 35% acetone-methanol. To ensure the HO^--reaction 1% of water was added to the CH_3O^- containing reaction solutions. Aside from the rate differences of the CH_3O^- and HO^- promoted reactions, the most remarkable effects are observed on the activation parameters which differ strongly in spite of almost identical reaction conditions. This seems strongly to indicate different mechanisms. We feel that the experimental data are best explained by postulating a rate determining pentacovalent anion intermediate in the HO^- reaction, and a hexacovalent rate determining intermediate in the CH_3O^- reaction:



Scheme 4

The activation energy is seen to be around 10 kcal/M lower for the CH_3O^- promoted decomposition, but the more favourable activation energy is counteracted by a much lower frequency factor (log *A*). The strong decrease in frequency factor is what might be expected from the above reaction Scheme 4 since the much more precise geometry, required for the hexacovalent route to be successful, decreases its probability as a reaction path.

EXPERIMENTAL

3-hydroxypropyl triphenyl phosphonium chloride was made from 30 g (0.125 M) triphenyl phosphine and 50 ml (0.6 M) 3-chloropropanol. The mixture was kept at 100°C for 2 hours. The precipitated salt was recrystallized several times from ether-ethanol mixtures, yield 75%, mp 224°C, Cl^-. Found: 10.03%, required: 9.94%.

Ethyl β-(diphenylphosphino)propionate[17] was made from ethyl acrylate, 6 g (0.06 M) and diphenylphosphine 8.8 g

TABLE III

Rates and activation parameters for the decomposition of tetraphenyl phosphonium bromide with CH_3O^- and HO^-

Solvent % acetone in methanol	Rate constants $k(l^2M^{-2}min^{-1})$		Activation parameters			
			E_{MeO^-}	E_{HO^-}	$\log (A\ l^2M^{-2}min^{-1})$	
	k_{MeO^-}	k_{HO^-}	kcal/M	kcal/M	$\log A^{50°}_{MeO^-}$	$\log A^{50°}_{HO^-}$
0	$0.00979^{50°}$ $0.02076^{55°}$	$0.0444^{60°}$ $0.326^{70.5°}$	32	43	17.9	27
25	$0.0676^{50°}$ $0.1329^{55°}$	$0.468^{49.8°}$ $2.80^{60.0°}$	29	38	16.6	25
35	$1.611^{50°}$ $2.985^{55°}$	$2.59^{49.8°}$ $17.9^{60.0°}$	26	41	16.3	28

(0.047 M) by mixing under nitrogen and heating at 130°C for 45° min 8.8 g ester (73%), bp 162°C/0.1 mm, $\nu_{C=O}$ = 1725 cm^{-1} was obtained P(Found): 10.70%, $C_{17}H_{19}O_2P$: 10.82%.

3-hydroxypropyl diphenyl phosphine was obtained from the previous ester, 57.8 g in 100 ml ether with equivalent amount of $LiAlH_4$. Yield 60.5%, mp 59°C[18]. ν_{HO} = 3375 cm^{-1}.

Di(3-hydroxypropyl)diphenyl phosphonium chloride was made from 3-hydroxypropyl diphenyl phosphine, 7.5 g, and 15 ml 3-chloropropanol by boiling the mixture for 2 hours. Yield: 5.2 g, mp 129°C (from ethanol–ethylacetate). ν_{HO} = 3350 cm^{-1}. $C_{18}H_{24}O_2PCl$: Found: C: 63.75, H: 7.10, P: 9.13. Required: C: 63.90, H: 7.15, P: 9.15.

Propyl triphenyl phosphonium iodide was made from triphenyl phosphine and *n*-propyliodide in dioxane. Recrystallized several times from ethanol, mp 297°C. $C_{21}H_{22}PI$, found: C: 58.40, H: 5.10, P: 7.12. Required: C: 58.34, H: 5.13, P: 7.16.

Tetraphenyl phosphonium bromide, triphenyl methyl phosphonium bromide and triphenyl 2-hydroxyethyl phosphonium chloride were synthesized and purified according to earlier descriptions.[4,7,19]

Solvents: All the solvents used were carefully dried and distilled before use. It is extremely important to get rid of the last traces of water in solvents and apparatus since otherwise the HO^- reaction will interfere with the alkoxide reaction.

Kinetic procedure: The kinetic measurements were performed as described earlier.[1,4,7,10] In the reaction with alkoxides all reaction vessels were well stoppered to prevent moisture to interfere with the measurements.

Reaction products were in the alkoxide as well as the hydroxyl promoted reactions found to be benzene and corresponding phosphine oxides.

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