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Ionization of Oxyphosphoranes. Phosphonium Ions and Hexacoordinated Phosphorus Anions

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Abstract: Conductivity measurements of purified phenoxyphosphoranes in dry acetonitrile allow the determination of the equilibrium constants the reactions 1 ($R_nP(OC_6H_5)_{5-n} \rightleftharpoons R_nP(OC_6H_5)_{4-n}{}^+ + C_6H_5O^-$ (K_1)) and 2 ($R_nP(OC_6H_5)_{6-n}{}^- \rightleftharpoons R_nP(OC_6H_5)_{5-n} + C_6H_5O^-$ (K_2)) with n = 1, 2, and 3. The formation of $P(OC_6H_5)_6{}^-$, an analogous anion, has been confirmed by ^{31}P NMR spectroscopy. The data have been combined with those for the rate of ionization of various phenoxyphosphoranes to show that the association of phenoxide ion and phosphonium ions in acetonitrile proceeds with the speed of collision.

The mechanism for the hydrolysis of phosphate esters requires the formation of pentacovalent intermediates which then decompose to products; in some instances, the hydrolysis is necessarily accompanied by a ligand reorganization (pseudorotation) of the trigonal bipyramidal intermediate.[1,2] One of the steps in the acid-catalyzed process is presumably the addition of water to a protonated ester:

$$(RO)_3POH^+ + H_2O \rightleftharpoons (RO)_3P(OH)_2 + H^+ \qquad (3)$$

The addition of a nucleophile to a phosphonium salt parallels the addition of water to a protonated phosphate ester, so that the rate and equilibrium of reactions such as (3) are needed for the full quantitative understanding of phosphate hydrolysis. Abundant qualitative evidence for the ionization of phosphoranes had previously been obtained[3] by NMR spectroscopy. The rates of dissociation of some phenoxyphosphoranes to phosphonium salts and phenoxide ion in acetonitrile as solvent have been measured by NMR spectroscopy.[4]

In order to obtain the corresponding rates of recombination of phenoxide ions with phosphonium ions, the equilibrium constants for the dissociations are needed. These have now been obtained by conductivity measurements in the same solvent. These measurements show, however, that the ionization is not a simple one, but is accompanied by the formation of hexacoordinated phosphorus anions. The ionization constants for the formation of these anions can also be obtained from the conductivity measurements and have been confirmed by ^{31}P NMR spectroscopy. This paper reports the determinations of some of these ionization constants and the calculations that can be based on the new data.

Experimental Section

General. The phosphonium salts and phosphoranes here described are sensitive to moisture and were routinely weighed and handled inside a Labconco drybox, filled with nitrogen. The effects of static electricity were minimized by a weak source of alpha particles (Staticmaster Ionizing unit, VWR Scientific No. 58580-041); transfers of solids were nearly impossible without it. The phosphoranes were recrystallized under nitrogen in a double Schlenk recrystallization tube (Ace Glass 7772-11); lesser precautions proved inadequate. The recrystallized compounds were stored under nitrogen at −20°.

Elementary microanalyses were performed by the Galbraith Laboratories, Inc., Knoxville, Tenn. Satisfactory analysis of triflate salts for sulfur could not be obtained by oxidation followed by precipitation of barium sulfate but were performed on a Leco Corp. sulfur analyzer. Melting points were obtained in sealed capillaries and are corrected. Variable-temperature proton NMR spectra were recorded on a Varian A-60 spectrometer equipped with a Varian V-6031B variable-temperature probe. The temperature was calibrated[5] by the spectrum of methanol or glycol. ^{31}P NMR spectra were obtained by Mr. W. E. Hull on a Varian XL-100 spectrometer at 40.5 MHz in Fourier transform mode. Chemical shifts for ^{31}P are recorded relative to that of 85% phosphoric acid, and those for protons relative to tetramethylsilane.

Materials. Sodium phenoxide[6] was dried in vacuo for at least a day at 69° and stored under nitrogen at −20°. Sodium triflate was purchased from Willow Brook.

Methyltriphenoxyphosphonium triflate[4] melted at 98.5-101.5°. Methyldiphenoxyphenylphosphonium triflate was prepared by stirring 18.2 g of diphenyl phenylphosphonite[4] and 10.1 g of methyl triflate in an ice bath under nitrogen. The exothermic reaction is rapid; the crystalline cake was broken under ether, and the solid was washed four times with ether and recrystallized under nitrogen from methylene chloride (about 8 ml/g) between its boiling point and −20°: mp 155.5-157.5°; NMR (acetone-d_6) δ 3.05 (d, $J_{\mathrm{H\text{-}P}}$ = 15 Hz, PCH_3), 6.8-8.6 (m, aromatic). Anal. Calcd for $C_{20}H_{18}F_3O_5PS$: C, 52.41; H, 3.96; P, 6.76; F, 12.43; S 6.99. Found: C, 52.46; H, 3.85; P, 6.67; F, 12.30; S, 7.11.

Methylphenoxydiphenylphosphonium triflate was prepared by slowly adding a solution of 5.98 g of methyl triflate (Willow Brook or Aldrich) in 10 ml of hexane to a stirred ice-cold solution of 10.1 g of phenyl diphenylphosphinite in 30 ml of dry ether under nitrogen. The heavy white precipitate, which formed immediately, was stirred for an hour at room temperature, filtered, washed with ether, and dried in vacuo; yield, 11.8 g (78%). The crude product can be recrystallized at −20° from 1,2-dichloroethane (1.7 ml/g). The salt melts at 100.5-102°: NMR ($CDCl_3$) δ 2.85 (d, $J_{\mathrm{H\text{-}P}}$ = 13 Hz, PCH_3), 6.8-8.3 (m, aromatic). Anal. Calcd for $C_{20}H_{18}F_3O_4PS$: C, 54.30; H, 4.10; P, 7.00; F, 12.88; S, 7.25. Found: C, 53.46; H, 3.86; P, 7.06; F, 13.09; S, 7.26. Phenyl trichlorophosphonium chloride melted at 69-77° (lit.[7] 75-76°).

Methyltetraphenoxyphosphorane was prepared by a modification of an earlier preparation.[4b] A solution of 10.6 g of methyltriphenoxyphosphonium triflate in 30 ml of methylene chloride was added by syringe through a serum cap in 5-ml portions under nitrogen to a stirred suspension of 2.58 g of sodium phenoxide in 25 ml of methylene chloride. The mixture was stirred for 2 hr at room temperature, and the fine precipitate was removed by filtration under nitrogen pressure. After the solvent had been removed from the filtrate, the resulting oil was crystallized from 10 ml of hexane at −20°. The product was then recrystallized in a double Schlenk recrystallization tube under nitrogen six times from 7:1 hexanes-benzene; half of it was then recrystallized three times more in the Schlenk tube from 25:1 hexanes:1,2-dichloroethane. The two samples melted at 82-84° and gave identical conductometric results. NMR ($CDCl_3$) δ 2.22 (d, $J_{\mathrm{H\text{-}P}}$ = 16 Hz), 6.7-7.3 (m, aromatic). Anal. Calcd for $C_{25}H_{23}O_4P$: C, 71.76; H, 5.54; P, 7.40. Found: C, 71.48; H, 5.75; P, 7.3.

Methylphenyltriphenoxyphosphorane. A solution of 7.09 g of methylphenyldiphenoxyphosphonium triflate in 75 ml of hot methylene chloride was added under nitrogen by syringe in 5-ml portions through a serum cap to a stirred slurry of 1.80 g of sodium phenoxide in 10 ml of methylene chloride. The mixture was stirred under nitrogen for 11.5 hr and was then filtered under nitrogen pressure. Evaporation of the filtrate yielded 5 g of a white solid that was recrystallized six times in the Schlenck tube under nitrogen from 30-ml portions of a 7:1 mixture of hexanes-benzene; about half of the sample was then further recrystallized three times in the Schlenck tube under nitrogen from 50-ml portions of 25:1 hexanes-dichloroethane. The two samples melted at 127-129.5° dec and gave identical conductometric results. Proton NMR ($CDCl_3$) δ 2.37 (broadened d, $J_{\mathrm{H\text{-}P}}$ = 14 Hz), 6.5-8.2 (m, aromatic); ^{31}P ($CDCl_3$) δ + 38.2. Anal. Calcd for $C_{25}H_{23}O_3P$: C, 74.62; H, 5.76; P, 7.70. Found: C, 74.74; H. 5.87; P, 7.58.

Methyldiphenyldiphenoxyphosphorane. A solution of 4.38 g of methyldiphenylphenoxyphosphonium triflate in 25 ml of methylene chloride was added under nitrogen by syringe through a serum cap to a stirred slurry of 1.21 g of sodium phenoxide in 25 ml of methylene chloride. The resulting mixture was stirred for 12.5 hr at room temperature and then filtered under nitrogen pressure. Evaporation of the filtrate at room temperature yielded 3.6 g of a white solid. This material was recrystallized in the Schlenk tube six times from 25-ml portions of 7:1 hexanes-benzene, and then half of the sample was further recrystallized three times from 25-ml portions of 25:1 hexanes-dichloroethane: mp 124.5-126.5° dec; NMR ($CDCl_3$) δ 2.45 (broad d, $J_{\mathrm{H\text{-}P}}$ = 15-16 Hz), 6.0-6.4, 6.4-7.1, 7.7-7.6, 7.7-8.5 (4 m's, aromatics); $^{31}P(CDCl_3)$ δ + 51.4.

The NMR spectrum of the phosphorane is temperature dependent; the methyl absorption sharpens at −12° to a clean doublet, δ 2.42 ($J_{\mathrm{H\text{-}P}}$ = 15 Hz), and coalesces to a singlet near +50°; this behavior parallels that discussed in the accompanying article.[4] Anal. Calcd for $C_{25}H_{23}O_2P$: C, 77.71; H, 6.00; P, 8.01. Found: C, 77.65; H, 6.02; P, 7.83.

Pentaphenoxyphosphorane and penta(*o*-cresoxy)phosphorane were synthesized by literature methods;[8,9] they melted at 111.5-113 and 112-117.5°, respectively.

Phenyltetraphenoxyphosphorane. A solution of 5.28 g of phenyltrichlorophosphonium chloride in 35 ml of carbon tetrachloride was added under nitrogen over 105 min to a stirred solution of 7.89 g of phenol and 8.98 g of 2,6-lutidine in 100 ml of dry ether at 0°. The ice bath was removed and the solution stirred overnight. The white precipitate was removed by filtration under nitrogen and washed with ether. The filtrate and washings were evaporated, and the residual oil was again dissolved in dry ether; a small amount of solid was filtered and the filtrate again evaporated. The residue was twice extracted with 25-ml portions of boiling hexanes, and the product partially crystallized at −20°. The resulting mixture of colorless solid and brown oil was separated by taking advantage of the fact that the oil dissolves much more rapidly than the solid in warm hexanes. The crude phosphorane had mp 124.5-129.5° dec. Anal. Calcd for $C_{30}H_{25}O_4P$: C, 74.99; H, 5.24; P, 6.45. Found: C, 74.69; H, 5.19; P, 6.19.

Acetonitrile. The solvent was purified and dried by a modification of the three-step "D-1" method of Coetzee et al.[10] Typically, a 1.8-l batch was stirred under nitrogen for 2-3 days with 18 g of calcium hydride, decanted, and distilled rapidly from phosphorus pentoxide through a 15-in. Vigreux column where a 50-ml forerun was discarded. The distillate was continuously refluxed over 9 g of calcium hydride until needed. Then it was distilled under nitrogen through a 13-in.-vacuum-jacketed column packed with glass helices at a reflux ratio of about 20:1. A 50-ml forerun was again discarded and the distillate collected in a special double-flask receiver, where the upper, 250-ml, two-necked flask was connected to the lower, 25-ml, pear-shaped three-necked flask through a medium-porosity fritted filter. Distilled acetonitrile was stored in the upper flask for as long as a week before use. Then, between 15 min and 2 hr before the solvent was to be used, 15 g of Woelm W-200 neutral alumina was added to the solvent in the upper flask. The acetonitrile was forced by nitrogen pressure from the upper flask into the lower and withdrawn by syringe through a serum cap.

Solvent prepared in this way had conductivity $K = 2\text{-}10 \times 10^{-8}$ ohm^{-1} cm^{-1}, values comparable to the best reported in the literature.[11,12] The water content was estimated as 6×10^{-4} *M* by Karl Fischer titration,[13] although the end point was not sharp at this low level of water. Attempts to determine water by VPC on Porapak Q were unsuccessful.

Solvents other than acetonitrile were dried over 4 Å molecular sieves. Diethyl ether was from freshly opened cans.

Methods. Conductivity measurements were made with a Serfass bridge, Model RC M15 (Arthur Thomas Co.), at 1000 Hz. The cell was a dip-type with parallel rectangular platinized platinum foil electrodes, about 1 cm^2 and separated by approximately 2 mm (Fisher, former 9-382; similar to current 9-324-26). The cell was modified by closing the bottom and vents and installing a side arm near the top for transfers of solution by syringe. The modified cell required 6.5 ml of solution to cover the electrodes to a depth where the conductivity became constant. The cell constant was 0.0986 cm^{-1} at 25.0 ± 0.1° and varied less than 2% over the period of this work. Solutions with resistances greater than about 150000 ohms were measured by putting a 107000- or 227000-ohm resistor in parallel with the cell. Measurement of such high resistances and of resistances less than 200 ohms was aided by adding up to 1 μF of auxiliary capacitance to the balancing arm of the bridge.

All volumetric flasks and syringes were washed with acetone and stored in an oven at 90°; the conductivity cell (except for determinations of cell constant) was washed only with acetonitrile and closed with serum caps. Syringes were calibrated gravimetrically and volumes determined gravimetrically where possible. Solutions were prepared in the drybox.

To conserve solutions, most samples were made up to 10 ml, which was not enough for duplicate experiments with the same sample. (Many duplicate experiments were carried out with separate samples.) For a partial verification of each experiment, 3 ml of the sample was withdrawn and replaced with the remainder of the solution. Samples from a given stock solution were run in order of increasing concentration to minimize the effect of contamination of one by any residue from the one before.

Table I. Limiting Molar Conductances of Some Salts in Acetonitrile at 25°

Cation	Anion	Λ_0, 10^{-3} ohm^{-1} cm^{-1} M^{-1}
$(PhO)_3P^+CH_3$	$CF_3SO_3^-$	156
$(PhO)_2P^+(CH_3)Ph_3$	$CF_3SO_3^-$	168
$PhOP^+(CH_3)Ph_2$	$CF_3SO_3^-$	155
Na^+	$CF_3SO_3^-$	151
Na^+	Picrate$^-$	147 (ref 17)
Na^+	Ph_4B^-	135 (ref 11)

Table II. Limiting Molar Conductances of Dissociated Phosphoranes Calculated from Values in Table I

Cation	Anion	Λ_0, 10^{-3} ohm^{-1} cm^{-1} M^{-1}
$(PhO)_3{}^+PCH_3$	PhO^-	152
$(PhO)_2{}^+P(CH_3)Ph$	PhO^-	164
$PhOP^+(CH_3)Ph_2$	PhO^-	151
$(PhO)_3P^+CH_3$	$(PhO)_5PCH_3^-$	140
$(PhO)_2P^+(CH_3)Ph$	$(PhO)_4PCH_3Ph^-$	152
$PhOP^+(CH_3)Ph_2$	$(PhO)_3PCH_3Ph_2^-$	139

Table III. Parameters of Least-Squares Lines Fit to Conductivity Data

Phosphorane	Intercept, M	Slope
$(PhO)_4PPh$[a]	$(3 \pm 5) \times 10^{-10}$	$(6.3 \pm 0.5) \times 10^{-7}$
$(PhO)_4PCH_3$	$(-2 \pm 37) \times 10^{-11}$	$(5.8 \pm 0.2) \times 10^{-7}$
$(PhO)_3P(CH_3)Ph$	$(7.8 \pm 4.0) \times 10^{-9}$	$(1.08 \pm 0.02) \times 10^{-5}$
$(PhO)_2P(CH_3)Ph_2$	$(5.3 \pm 0.3) \times 10^{-6}$	$(2.2 \pm 0.3) \times 10^{-4}$

[a] The figures reported for this compound were determined on only one run on one sample.

Results

Ionization of the Phosphoranes. The conductivity of the phosphoranes was determined in dry acetonitrile at 25.0 ± 0.1°, and the results were used to calculate an "ionization constant", K. This constant proved to increase with increasing concentrations of phosphorane; obviously then, the system could not be represented only by the equilibrium of eq 1. The data have, however, been analyzed successfully in terms of the two equilibria represented by eq 1 and 2.

$$R_nP(OC_6H_5)_{5-n} \overset{K_1}{\rightleftharpoons} R_nP(OC_6H_5)_{4-n}{}^+ + C_6H_5O^- \quad (1)$$

$$R_nP(OC_6H_5)_{6-n}{}^- \overset{K_2}{\rightleftharpoons} R_nP(OC_6H_5)_{5-n} + C_6H_5O^- \quad (2)$$

In these equations, the groups, R, may be methyl, phenyl, or combinations of them.

In order to determine the value of the variable, K, it was necessary to measure the conductivity of the phosphorane and to estimate the limiting conductance of the phosphonium phenoxides. The standard procedure is to determine the limiting molar conductances Λ_0 (extrapolated to zero concentration) of appropriate salts, such as phosphonium triflates, and sodium phenoxide. This proved impractical; sodium phenoxide is incompletely ionized in acetonitrile as solvent. Its molar conductance at 0.01 M (in 10^{-3} ohm^{-1} cm^{-1} M^{-1}) was only about 5, and rose in more dilute solutions no higher than about 50; in the most dilute solutions (where the concentration of salt approached that of the residual water in the solvent), the conductance actually fell from this value. By contrast, fully dissociated salts have molar conductances in acetonitrile of around 150 (see Table I). (Alkali metal phenoxides are also highly associated in 1,2-dimethoxyethane and in dimethylformamide.[14]) Attempts to overcome these difficulties by preparing crown ether[15] chelates of the phenoxides that would be stable in acetonitrile were unsuccessful.[16] The assumption was therefore made that the known limiting conductance of sodium picrate[17] in acetonitrile would not differ greatly from that of sodium phenoxide. Similarly, we needed the limiting conductance of a hexacovalent phosphorus anion (in particular, $(C_6H_5O)_6P^-Na^+$), and approximated this value by the known[11] limiting conductance of $(C_6H_5)_4B^-Na^+$, on the assumption that the limiting conductance of all large anions is similar. The limiting molar conductances of some salts in acetonitrile at 25° are presented in Table I; the limiting molar conductances of three phosphoranes and of three salts of hexacoordinated phosphorus anions, calculated from these data, are shown in Table II.

A quantity K_a was calculated (a) as if the ionization of eq 1 were the only process that occurs, with the aid of the additional assumptions, (b) that all activity coefficients were unity, and (c) that the extent of ionization is small. K_a then is an approximation to K_1 and is a better or worse approximation depending on the extent to which the primary assumption (a) above is valid. Although this assumption turns out to be quite poor, K_a nevertheless provides a useful parameter from which K_1 and K_2 can be obtained. In the examples here considered and under our experimental conditions, the approximations introduced by (b) and (c) are not important. In fact, the value of K_a does not differ by more than 3% from the more nearly exact value than can be obtained[16] by taking into account both the activity coefficients of ions in acetonitrile[12,18] and the effect on the calculated concentration of phosphorane of the small extent of its dissociation. In practice, K_a was calculated from the simple equation

$$K_a = c(\Lambda/\Lambda_0)^2 \quad (4)$$

where c is the concentration of the phosphorane. The results obtained with three rigorously purified phosphoranes are presented in Figures 1-3. For these compounds (methyltetraphenoxyphosphorane, methylphenyltriphenoxyphosphorane, and methyldiphenyldiphenoxyphosphorane), conductivity measurements were repeated many times with many different samples, recrystallized both from benzene-hexanes and from dichloroethane-hexanes. In general, quite convincing and reproducible results were obtained, although those for methyldiphenyldiphenoxyphosphorane (the most hydrolytically labile of these compounds) show ±15% scatter. The concentrations of phosphorane used in the calculations of K_a have been corrected for the presence of 6×10^{-4} M water in the solvent by assuming quantitative hydrolysis; the corrections were generally small, and the contribution of the hydrolysis products to the conductivity proved negligible. The slope and intercet for the plots of K_a against c are given in Table III, together with the data for less thorough experiments with phenyltetraphenoxyphosphorane. The two pentaaryloxyphosphoranes (the pentaphenoxy and pentacresoxy compounds) had negligible conductivities, so that the upper limit for their K_a's is around 10^{-10} M.

Interpretation of the Data. The increase in K_a with increasing concentration of phosphoranes shows that some ion-forming process with second or higher order dependence upon concentration must be operative. All of the data can in fact be accounted for by assuming that phosphoranes ionize in accordance with eq 2 as well as with eq 1. The derivation presented in the Appendix leads to the conclusion that, under these assumptions,

$$K_a = [K_1 + K_3c(\Lambda_0'/\Lambda_0)]^2/(K_1 + K_3c) \quad (5)$$

where $K_3 = K_1/K_2$, and Λ_0' is the limiting conductance of a

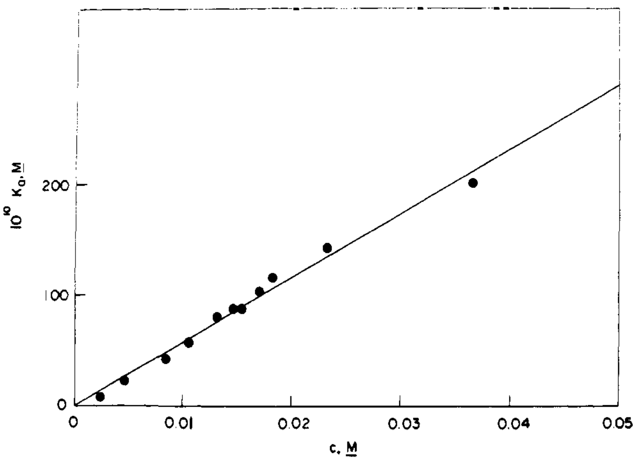

Figure 1. Apparent dissociation constant of methyltetraphenoxyphosphorane, determined conductometrically at 25° in acetonitrile as solvent, plotted against the concentration of the phosphorane.

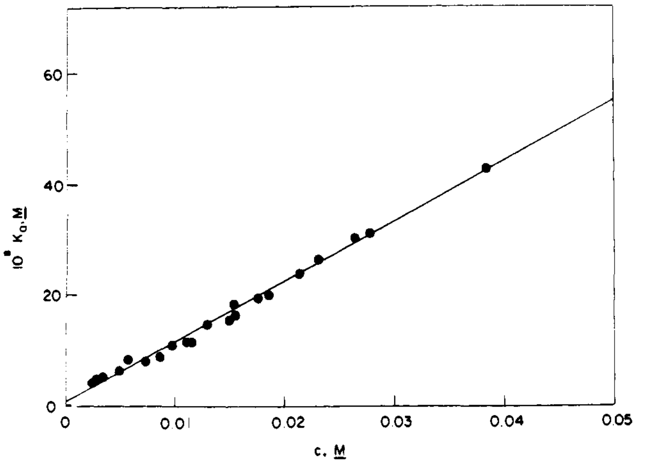

Figure 2. Apparent dissociation constant of methylphenyldiphenoxyphosphorane, determined conductometrically at 25° in acetonitrile as solvent, plotted against the concentration of the phosphorane.

phosphonium salt of a hexacoordinated phosphorus anion. If $\Lambda_0 = \Lambda_0'$, then

$$K_a = K_1 + K_3c \qquad (6)$$

The experimental plots of K_a against c are in fact linear, and to the extent that the limiting conductances of a given phosphonium picrate approximates that of the corresponding phosphonium salt of a hexacoordinated phosphorus anion (i.e., to the extent that Λ_0 is a good approximation to Λ_0'), eq 6 can be used as an approximation to eq 5. K_1 and K_3 are then the intercept and slope, respectively, of the lines in Figures 1-3.

However, if the tetraphenylborate ion is, as we have assumed, a good model for a hexacoordinated phosphorus anion, then the ratio of Λ_0' to Λ_0 for the various salts is about 0.925 rather than 1.000. Equation 5 cannot easily be solved explicitly when Λ_0'/Λ_0 differs from unity. Since, however, the ratio of Λ_0' to Λ_0 is close to unity, one can expand the quotient $[K_1 + K_3c(\Lambda_0'/\Lambda_0)]^2/(K_1 + K_3c)$ in series and discard terms after the second as negligible. When Λ_0'/Λ_0 is 0.925, to a good approximation (i.e., with an error in slope of less than 1%)

$$K_a = K_1 + K_3c(\Lambda_0'/\Lambda_0)^2 = K_1 + 0.84K_3c \qquad (7)$$

The curves of Figures 1-3 and eq 7 lead to the data in Table IV.

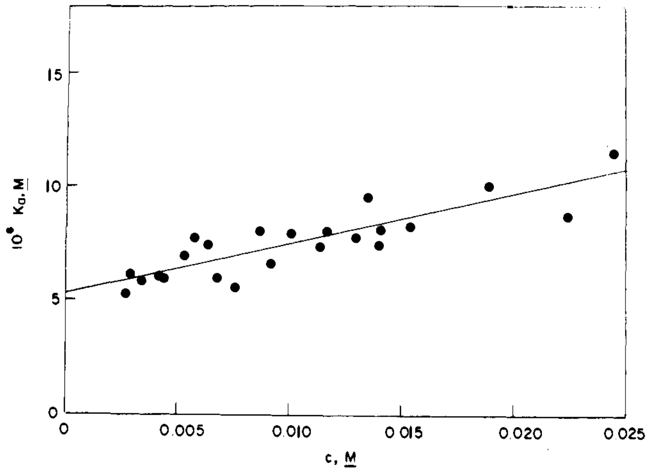

Figure 3. Apparent dissociation constant of methyldiphenyldiphenoxyphosphorane, determined conductometrically at 25° in acetonitrile as solvent, plotted against the concentration of the phosphorane.

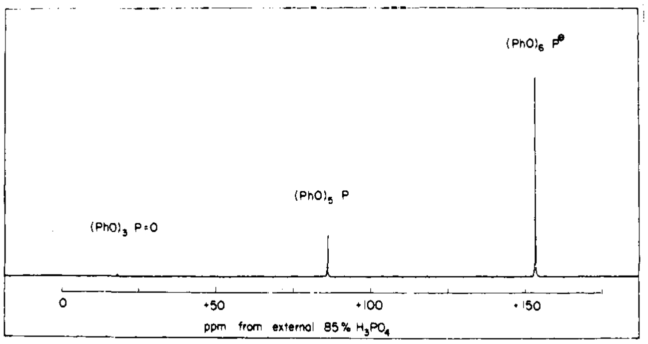

Figure 4. The 40.5-MHz proton-decoupled Fourier transform ^{31}P NMR spectrum of an equimolar mixture of pentaphenoxyphosphorane and sodium phenoxide, determined at room temperature in 4:1 dimethylformamide-trideuterioacetonitrile as solvent.

Table IV. Equilibrium Constants of Reactions of Phosphoranes

Phosphorane	K_1, M	K_2, M	$K_1/K_2 = K_3$
$(PhO)_4PPh$	$(3 \pm 5) \times 10^{-10}$	$<1 \times 10^{-3}$	$(7.5 \pm 0.5) \times 10^{-7}$
$(PhO)_4PCH_3$	$<4 \times 10^{-10}$	$<5 \times 10^{-4}$	$(6.8 \pm 0.4) \times 10^{-7}$
$(PhO)_3P(CH_3)Ph$	$(8 \pm 4) \times 10^{-9}$	$4.2-12 \times 10^{-3}$	$(1.26 \pm 0.04) \times 10^{-5}$
$(PhO)_2P(CH_3)Ph_2$	$(5.3 \pm 1.0) \times 10^{-6}$	$1.2-4.8 \times 10^{-2}$	$(2.7 \pm 1.3) \times 10^{-4}$

Verification of the Equilibrium Controlled by K_a. The equilibrium constant for the dissociation of $CH_3P(OC_6H_5)_5^-$ to the phosphorane and phenoxide ion is less than 1×10^{-3} M; this indicates that the phosphorane and phenoxide ion, if mixed at moderate concentrations, would react substantially to yield the anion. The trend of the equilibrium constants with substitution is such as to suggest that the equilibrium would be even more favorable for the formation of $P(OC_6H_5)_6^-$; this dissociation constant might be as small as 2×10^{-5} M. Unfortunately, no source of free phenoxide ion in acetonitrile is yet available; the conductivity of sodium phenoxide suggests a dissociation constant for that salt of only 4×10^{-5} M. Although these numbers are highly approximate, one can crudely estimate that equimolar solutions of sodium phenoxide and of pentaphenoxyphosphorane in acetonitrile should be converted to the extent of about 60% to the hexacoordinated anion.

This prediction has been verified by ^{31}P NMR spectroscopy, as shown in Figure 4. The signal from the anion ap-

Table V. Calculated Rate Constants for Attack of Phenoxide Ion on Phosphonium Ions in Acetonitrile Near 25°

Phosphonium Ion	k_d, sec^{-1}	K_1, M	k_a, M^{-1} sec^{-1}
$(PhO)_3{}^+PCH_3$	7.5[a]	4×10^{-10}	1×10^{10}
$PhOP^+(CH_3)Ph_2$	10^4[b]	5.3×10^{-6}	2×10^9

[a] Interpolated from data of ref 4 at 23 and 45°. [b] Estimated by extrapolating the data of ref 4 for the reaction in THF-d_8 from −45 to +25°, and then multiplying by a factor of 5.33 to take into account the difference in rate caused by difference in solvent. This factor was determined experimentally at 25° for methyltetraphenoxyphosphorane; it is here assumed to be the same for methyldiphenyldiphenoxyphosphorane.

pears at +153 ppm, relative to that of 85% phosphoric acid, and constitutes at least the major portion of the phosphorus signal. The unreacted phosphorane gives rise to the signal at +86 ppm. The tiny signal at +18 ppm is real; it arises from the triphenylphosphate formed by hydrolysis of the phosphorane by the trace of moisture introduced with the "dry" sodium phenoxide; this experiment illustrates graphically the extent to which the solutions used in this research approached being anhydrous. The position of the signal from $(C_6H_5O)_6P^-$ (at +153 ppm) is approximately where it would be expected by extrapolation from the data that have been published for various isolated hexacoordinated phosphorus anions.[19]

The equilibrium constant and perhaps the chemical shifts are, however, subject to some uncertainties, since the solvent was a 4:1 mixture of DMF and acetonitrile (rather than acetonitrile, as used in the conductometric studies); this modification was needed to obtain the concentrations required for easy ^{31}P NMR measurements.

Discussion

The data of Table IV are consistent with the assertion that the phosphoranes are weakly dissociated in acetonitrile as solvent. The dissociations of the tetraoxy-substituted phosphoranes are on the limit of measurement, while the pentaoxyphosphoranes do not dissociate enough to measure by our methods. The rate constants for the associations of phosphonium ions and phenoxide ions can now be calculated for the two phosphoranes for which both NMR and conductivity data are available. The rate constants, k_d, have been measured by NMR measurements;[4] since $k_a = k_d/K_1$, the pertinent data for k_a can be calculated and are presented in Table V. The rate constants for association in both cases are near the diffusion limit. When these data have been extended to other solvents and other nucleophiles, they will provide the intimate details needed for understanding of the mechanism of the hydrolysis of phosphates through pentacovalent intermediates.

Moreover, in addition to these data pertaining to pentacovalent intermediates, the present investigation offers some quantitative information concerning the formation of hexacoordinated phosphorus anions in acetonitrile as solvent. The small dissociation constants observed for these hexacoordinated phosphorus anions reinforces the suggestion of Gillespie,[20] Ramirez,[21] and coworkers that hexacoordinated phosphorus anions may be involved in some of the hydrolyses of esters of acids of phosphorus. The hydrolysis of pentaaryloxyphosphorane had previously been shown to proceed[8] by way of hexacoordinated anions. Furthermore, the dissociation constants of the hexacoordinated anions, shown in Table IV, are smaller the greater the number of oxygen substituents attached to phosphorus. That is to say, the probability of the intervention of hexacoordinated anions is greatest in the hydrolysis of phosphates (the case of greatest biological interest) as contrasted to the hydrolysis of phosphonates and phosphinates. Although the difference in solvent properties between water and acetonitrile is too great to permit much confidence in extrapolation—either for the pentacoordinated or hexacoordinated species—the present work shows that the intervention of hexacoordinated intermediates in the hydrolysis of phosphate esters must be given increased credence and may, under some experimental conditions, provide a pathway for the hydrolysis of phosphate esters, although pentacoordinate intermediates presumably provide the major pathway in most cases.

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Appendix

Let P^4 stand for a phosphonium salt, P^5 for a phosphorane, and P^6 for a hexacoordinated phosphorus anion. Then

$$(P^4)(PhO^-)/(P^5) = K_1 \qquad (1)$$

$$(P^5)(PhO^-)/(P^6) = K_2 \qquad (2)$$

Electroneutrality and conservation of phosphorus lead to

$$(P^4) = (P^6) + (PhO^-) \qquad (8)$$

$$(P^4) + (P^5) + (P^6) = c \qquad (9)$$

Eq 1, 2, 8, and 9 can be reduced to (10), a cubic equation in (P^5)

$$A_3(P^5)^3 + A_2(P^5)^2 + A_1(P^5) + A_0 = 0 \qquad (10)$$

where $A_3 = (K_2 - 4K_1)/K_2{}^2$; $A_2 = (K_2 - 2c - 4K_1)/K_2$; $A_1 = (c^2 - 2cK_2 - K_1K_2)/K_2$, and $A_0 = c^2$. Given trial values of K_1 and K_2, this cubic can be solved for the concentration of P_5, and the other concentrations then obtained from eq 1, 2, 7, and 8 above. A computer program was developed[16] to solve the cubic.

An important special case, applicable to the present research, arises when the fraction of a compound that is dissociated is very much less than unity. Then, to a good approximation, $(P^5) = c$, and (with $K_3 = K_1/K_2$)

$$(P^4) = \sqrt{K_1c + K_3c^2};\ (P^6) = K_3c^2/\sqrt{K_1c + K_3c^2} \qquad (11)$$

and

$$(PhO^-) = K_1c/\sqrt{K_1c + K_3c^2}$$

If we then define λ_i as the specific molar conductance of the ith ion, and κ as the conductance of the solution,

$$10^3\kappa = \lambda_4(P^4) + \lambda_6(P^6) + \lambda_{PhO^-}(PhO^-) \qquad (12)$$

Since $\lambda_4 + \lambda_{PhO^-} = \Lambda_0'$, and $\lambda_4 + \lambda_6 = \Lambda_0'$,

$$10^3\kappa = c(\Lambda_0K_1 + \Lambda_0'K_3c)/\sqrt{K_1c + K_3c^2} \qquad (13)$$

From the definition of K_a (eq 4) and of Λ, it follows that

$$K_a = c(\Lambda/\Lambda_0)^2 = c(10^3\kappa/\Lambda_0)^2 \qquad (14)$$

Equations 13 and 14 lead directly to eq 5 for the special case under consideration. The approximation of eq 5 by eq 7 has already been given.

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Rates of Ionization of Phosphoranes

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Abstract: The rates of ionization of $CH_3P(OC_6H_5)_4$ and of several related phosphoranes have been measured by NMR spectroscopy. The equilibrium $CH_3P(OC_6H_5)_4 \rightleftharpoons CH_3P(OC_6H_5)_3{}^+ + C_6H_5O^-$ (1) is displaced so far toward the left that the ionic products cannot be seen by available NMR techniques, but the spectrum of an equimolar mixture of the phosphorane and of the related phosphonium triflate, $CH_3P(OC_6H_5)_3{}^+CF_3SO_3{}^-$, proved to be temperature dependent. Line-shape analyses of these spectra then permit a determination of the rate constant for the dissociation of the phosphorane; temperature-dependent NMR spectra and the corresponding rate constants were also obtained for 1:1 mixtures of $CH_3P(C_6H_5)(OC_6H_5)_3$, of $CH_3P(C_6H_5)_2(OC_6H_5)_2$, of $CH_3P(o\text{-}OC_6H_4CH_3)_4$, and of $CH_3P(p\text{-}OC_6H_4CH_3)_4$ with the corresponding phosphonium cations. Equilibrium constants for some of these reactions have been obtained by conductometric measurements,[2] so that the rate constants for the association of phosphonium cations and phenoxide ion could then be calculated. The relationship of these data to the mechanism for the hydrolysis of phosphate esters is discussed.

The hydrolysis of phosphate esters, in many cases, takes place by way of a trigonal-bipyramidal phosphorane as intermediate.[3-5] An essential step in the formation of the intermediate in acid solution is presumably the addition of water to a protonated ester molecule (eq 2 and 3). The rate constants of reaction 3 are not yet available or susceptible of easy measurement. In order to investigate the rates and equilibria of related additions of nucleophiles to phosphonium salts, some of the physical-organic chemistry of stable phosphoranes has been investigated. This investigation, then, represents a first step in a program aimed, eventually, at a determination of the rate constants of eq 3. In particular, the NMR spectra of several phosphoranes dissolved in various solvents (CD_2Cl_2, THF-d_8, CD_3CN) have been investigated in the hope of observing the equilibrium between salt and phosphorane (eq 1).

$$CH_3P(OC_6H_5)_4 \rightleftharpoons CH_3P(OC_6H_5)_3{}^+ + C_6H_5O^- \quad (1)$$

$$(RO)_3P{=}O + H^+ \rightleftharpoons (RO)_3P^+OH \quad (2)$$

$$(RO)_3P^+OH + H_2O \underset{k_d}{\overset{k_a}{\rightleftharpoons}} (RO)_3P(OH)_2 + H^+ \quad (3)$$

If these NMR spectra had proved temperature dependent, they might have provided information leading to determination of the rates of the relevant processes. Unfortunately, the equilibria in reaction 1 and in other similar reactions lie so far in favor of the phosphoranes that, starting with pure phosphorane, only signals from these compounds could be detected. However, in favorable cases, when solutions of a phosphorane and of the corresponding phosphonium trifluoromethanesulfonate ("triflate") are mixed, the signals from the methyl groups of cation and phosphorane are both present at low temperatures, but coalesce at higher temperatures.

The experiments here recorded were carried out by two more or less equivalent methods. In the best experiments, the phosphorane and phosphonium triflate were separatedly purified, and then a solution of equivalent quantities of these materials was prepared in a drybox in a suitable solvent, usually trideuterioacetonitrile. In other experiments, a weighed amount of a trifluoromethanesulfonate salt was dissolved or suspended in a solvent with half the molar amount of sodium phenoxide. When the solvent for the reaction was bromobenzene or deuterated methylene chloride, sodium triflate proved insoluble, and could be removed by centrifugation:

$$R_nP(OAr)_{4-n}{}^+\,CF_3SO_3{}^- + Na^+ArO^- \rightleftharpoons R_nP(OAr)_{5-n} + CF_3SO_3Na \quad (4)$$

On the other hand, sodium triflate is soluble in deuterated tetrahydrofuran; the reaction nevertheless was carried to completion, even when the phosphonium salts were nearly insoluble in the solvent, because of the favorable equilibria for the formation of the phosphoranes. Incidentally, triflate salts were chosen because they are essentially nonnucleophilic. Some experiments were conducted successfully with fluoroborates; in other cases, the decomposition of this anion to yield BF_3 occasioned difficulties.[6]

The temperature-dependent NMR spectra of mixtures of phosphonium salt and phosphorane permit the measure-